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Vol. XXXVI.

1879. ABSTRACTS.

LONDON:
J. VAN VOORST, 1, PATERNOSTER ROW.
1879.

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CONTENTS.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

General and Physical Chemistry.

PAGE

VOGEL (H. W.). Differences in the Absorption Spectra of one and the same Substance 1

LECLANCHÉ. An Improvement in the Peroxide of Manganese Battery . . 1

HITTORF (W.). Proof of the Statement that "Electrolytes are Salts," a Reply to L. Bleekrode 1

WULLNER (A.). Relation between the Specific Heat at a constant Volume, the Temperature, and the Conductivity of Gases 2

CLAUSIUS (R.). The Relation between Work effected by the Diffusion of Gases and the Second Law of Thermodynamics 3

RAOULT (F. M.). Vapour-tension and Solidifying Point of Saline Solutions . 4

OGIER (J.). Measurement of the Heat developed in the Formation of Hydrogen Phosphides and Arsenides 5

THOMSEN (J.). Thermo-chemical Researches: Heat of Solution of Nitrates, Sulphates, Dithionates, and some other Salts 6

CIAMICIAN (G.). Influence of Temperature and Pressure on the Spectra of Gases 101

BURGER (H.). Spectroscopic Investigation of the Constitution of Liquids . 101

LANDAUER (J.). Absorption Spectra 101

BÖTTGER (R.). Planté's Secondary Battery 101

BÖTTGER (R.). Production of Rotatory Movements in Mercury . . . 102

BÖTTGER (R.). Production of a High Temperature by means of Ammonium Nitrate 102

MOHR (F.). Material for Standard Weights and Measures 102

VOGEL (H.). Difference of the Absorption-spectra of one and the same Substance 189

KIRMIS (M.). Transference of the Ions 193

BRAUN (F.). Unipolar Electrolytic Conduction 194

HERWIG (H.). On the Quantity of Electricity necessary for the Complete Charge of a Platinum-water Cell, and the Distance between the Molecules of Liquid Water 194

THOMSEN (J.). Monohydrated Sodium Sulphate and Dehydrated Sodium Carbonate 194

RITTER (A.). The "Temperature Surface" of Carbonic Acid . . . 195

NAUMANN (A.). Density and Decomposition of Nitric Acid . . . 195

BÖTTINGER (C.). Dissociation of Ammonium Chloride, a Lecture Experiment 196

HOFMANN (A. W.). Modified Vapour-density Determination . . . 196

TILDEN (W. A.). Determination of Specific Gravities 197

SCHRÖDER (H.). Law of Molecular Volumes 197

SCHRÖDER (H.). Law of Molecular Volumes 198

ULLIK (F.). Gelatinous Silica as an Inorganic Membrane 199

BOUVET (A.). Electro-chemical Actions under Pressure 293

CROVA (A.). Spectrometric Measurement of High Temperatures . . . 293

VIOLLE (J.). Specific Heat and Latent Heat of Fusion of Palladium . . 294

CRESTI (L.). Gas Regulator for Air-baths 294

MEYER (V. and C.). Determination of Vapour-densities of Substances which attack Mercury, or which boil above 440° 294

B 8056

PAGE

VINCENT (C.) and DELACHANAL. Density and Coefficient of Expansion of Liquid Methyl Chloride 294
CLARKE (F. W.). Specific Gravity Determinations 295
BERTHELOT. Reciprocal Displacements between Oxygen, Sulphur, and the Halogens when combined with Hydrogen 296
BERTHELOT. Reaction between Mercury and Hydrochloric Acid Gas . . 298
NARR (F.). Behaviour of Electric Currents in Rarefied Gases . . . 345
BEETZ (W.). Excitation of Electricity by the Contact of Solid and Gaseous Bodies 345
DORN (E.). Electrical Currents produced by the flow of Liquids through Tubes 346
WINKELMANN (A.). Deviation of some Gases from Boyle's Law . . . 346
STÄDEL (W.) and E. HAHN. Apparatus for Regulating the Atmospheric Pressure in Boiling-point Determinations 346
STEFAN. Diffusion of Carbonic Anhydride through Water and Alcohol . 347
LEBAIGNE (E.). Apparatus for Continual Dialysis 347
WIEDEMANN (G.). Dissociation of Dissolved Ferric Salts 348
OSWALD (W.). Chemical Affinity 348
BERTHELOT. Relative Affinities and Reciprocal Displacements of Oxygen and the Halogen Elements 351
MEYER (F.) Preparation of large regular Crystals 352
CONROY (Sir J.). The Light reflected from Potassium Permanganate . . 425
LOCKYER (J. N.). Recent Researches in Solar Chemistry 425
BROWN (J.). Theory of Voltaic Action 426
HÉRAUD (A.). New Voltaic Element with Constant Current . . . 426
AYRTON (W. E.). Electrical Properties of Beeswax and Lead Chloride . 427
GUTHRIE (F.). On Salt Solutions and Attached Water 428
CAILLETET (L.). Compressibility of Gases 429
SCHRÖDER (H.). Law of Molecular Volumes 430
SABINE (R.). Motions produced by Dilute Acids on some Amalgam Surfaces 431
WITZ (A.). Thermic Effect of the Walls of Closed Vessels on the Contained Gases 432
THOMSEN (J.). Accuracy of Thermo-chemical Results 433
THOMSEN (J.). Heat of Formation of Metallic Sulphides 433
BERTHELOT. Formation of Haloïd Ethers in the Gaseous State . . . 435
VOGEL (H. W.). Photographed Spectra of Oxygen and Hydrogen . . 497
SMITH (A. P.). Blue Flame from Common Salt 497
RODWELL (G. F.) and H. M. Elder. Effect of Heat on Mercury Diiodide . 498
PECKHAM (E. F.). Determination of Specific Gravities 498
PFAUNDLER (L.). Vapour-density Determinations at High Temperatures of Substances which attack Mercury 499
BRÜHL (J. W.). Limits to the application of the Method of determining Vapour-densities in the Barometric Vacuum 499
ENGEL (B.) and MOITESSIER. Dissociation of Chloral Hydrate . . . 500
SMITH (R. A.). Absorption of Gases by Charcoal. Part II. On a New Series of Equivalents or Molecular Numbers 500
GRENFELL (J. G.). Supersaturated Solutions 501
BAYLEY (T.). Catalysis 501
CROOKES (W.). Illumination of the Lines of Molecular Pressure, and the Trajectory of Molecules 573
VIOLLE (J.). Radiation from Incandescent Platinum 573
LEPEL (B. F. v.). New Universal Stand for use with the Pocket Spectroscope 574
THOLLON (L.). Displacement of the Lines of the Spectrum by the Motion due to the Sun's Rotation 574
MELDOLA (R.). A Cause for the Appearance of Bright Lines in the Solar Spectrum 574
LOCKYER (J. N.). Researches on Spectra 575
VILLARI (E.). Thermic and Galvanometric Laws of the Electric Spark . 576

PAGE

Beilstein (F.) and L. Jawein. Treatment of Bunsen's Cells . . . 576
Bouty. Pressures produced by Galvanic Deposits 576
Becquerel (H.). Magnetic Rotatory Power of Gases at Ordinary Temperature and Pressure 576
Bichat (E.). Magnetic Rotatory Power of Vapours 577
Exner (F.). Electrolysis of Water: Galvanic Polarisation 577
Exner (F.). Galvanic Polarisation of Platinum in Water 578
Calm (A.). Vapour-density of Aqueous Acids with Constant Boiling Points 579
Meyer (C. and V.). Vapour-densities of some Inorganic Bodies . . . 579
Mohr (F.). Nature of Cohesion and its Chemical Signification . . . 579
Hermann (R.). Specific Gravity and Atomic Volume of the Cerium Metals 579
Guldberg and Waage. Chemical Affinity 580
Stohmann (F.). A Calorimetric Method 586
Mitscherlich. On New Phenomena shown by Gases 587
Mills (E. J.). Researches in Thermometry 588
Carnelley (T.). Relation between the Melting Points of the Elements and their Coefficients of Expansion by Heat 588
Rechenberg (V.). Heat-absorption attending the Solution of Potassium Chloride in Water 588
Coppet (L. C. de). Heat developed by Contact of Water with Anhydrous Sodium Sulphate 589
Berthelot. Decomposition of Haloïd Acids by Metals 589
Beketoff (M.). Determination of the Atomic Heat of Hydrogen in its Combination with Palladium 590
Berthelot. Combination of Carbonic Oxide with the Elements . . . 591
Ciamician (G.). Spectra of the Elements and their Compounds . . . 685
Ciamician (G.). Influence of Temperature and Pressure on the Spectra of Vapours and Gases 685
Auerbach (F.). The Passage of the Galvanic Current through Iron . . 686
Puschl (C.). Sketch of the Atomic Theory of Heat 687
Donath (J.). Specific Heat of Uranoso-uranic Oxide, and the Atomic Weight of Uranium 688
Lecher (E.). Heat-capacity of Mixtures of Methyl Alcohol and Water . 688
Hammerl (H.). Freezing Mixture of Calcium Chloride and Snow . . 689
Lorin (M.). Preliminary Study of the Action of Acids on Salts without the Intervention of a Solvent 689
Beketoff. Heat of Hydration of Sodium Oxide, and the Action of Sodium Hydroxide and of Hydrogen on Sodium Oxide 689
Wiebe (H. F.). Thermo-chemical Relation between the Boiling and Melting Points of Solid Elements 690
Naumann (A.). Dissociation of Chloral Hydrate 690
Kessler (F.). Law of Multiple Proportions 691
Abt (A.). Continuous Spectrum of the Electric Spark 765
Goldstein (M.). Boiling Points of Normal Ethanes (Paraffins) . . . 765
Meyer (V. and C.). Vapour-density Determinations of Inorganic Bodies at High Temperatures 766
Berthelot. Heat of Formation of Cyanogen 767
Ogier (J.). Thermic Formation of Silicon Hydride 767
Ogier (J.). Thermic Researches on Silicic Ether 767
Louguinine (W.). Influence of Substitution on the Evolution of Heat during Formation of Salts 767
Schröder (H.). Volume-constitution of the Sulphates, Selenates, and Chromates of the Magnesium Metals 768
Kopp (H.). Determination of Atomic Weights, and the Use of Isomorphism for the same 769
Cornu (A.). Ultra-Violet Limit of the Solar Spectrum 861
Paalzow (A.). The Oxygen Spectrum and Luminous Appearance of Rarefied Gases in Tubes with Liquid Electrodes 861
Boisbaudran (L. de). Spectrum of Ytterbium 861

PAGE

Smith (J. L.) and L. de Boisbaudran. Spectrum of Didymium Nitrate . 861
Boisbaudran (L. de). Spectrum of Erbium Nitrate 862
Lamansky (S.). Stokes's Law 862
Becquerel (E.). On a Note by Lamansky on Stokes's Law . . . 862
Soret (J. L.). Fluorescence of the Salts of the Earth-metals . . . 862
Baudrimont (A.). Influence of Coloured Light on the Evaporation of Water 863
Freund (C.). Some Galvanic Properties of Aqueous Solutions of Metallic Salts 863
Beetz (W.). Electric Conductivity of Zinc Sulphate Solution . . . 864
Blondlot (R.). Capacity of Voltaic Polarisation 864
Desains (P.). Refraction of Invisible Heat 864
Berthelot. Amalgams of the Alkali-metals, and the Nascent State . . 864
Sabatier (P.). Thermo-chemical Study of the Alkaline Sulphides . . 865
Sabatier (P.). Thermo-chemical Study of Dissolved Alkaline Sulphides . 866
Berthelot. Etherification 866
Louguinine (W.). Thermic Effect of Substitutions 871
Berthelot. Some Thermo-chemical data 874
Berthelot. Observations on Noble and Abel's Memoir on the Combustion of Gunpowder 875
Meyer (V. and C.). Vapour-densities of some Inorganic Compounds . . 875
Pictet (R.). Study of the Molecular Constitution of Liquids by means of their Coefficient of Dilation, Specific Heat, and Atomic Weight . . 875
Exsiccator for Carbon Bisulphide, Ether, Chloroform, and Benzene . . 875
Troost (L.). Distillation of a Heterogeneous Liquid 875
Guyard (A.). Viscosity, a cause of Catalysis 876
Mills (E. J.) and J. J. Smith. Researches on Chemical Equivalence . . 876
Attenkofer (G.). A Simple Gasholder 877
Draper (J. C.). Presence of Dark Lines in the Solar Spectrum which correspond closely with the Oxygen Lines 997
Gernez (D.). Distillation of Liquids under the Influence of Static Electricity 997
Edlund (E.). The Electromotive Force produced by the Flow of Liquids through Tubes 998
Riecke (E.). The Electromotive Power of a Grove's-element in Terms of Siemens-Weber Units 998
Pierce (B. O.). The Electromotive Power of Gas Elements . . . 998
Barus (C.). The Thermoelectric Position and Electric Conductivity of Steel in their Relation to its Hardness 999
Waltenhofen (A. v.). Magnetic Behaviour of Finely-divided Iron . . 1000
Beetz (W.). Conductivity of Liquids for Heat 1001
Henrichsen (S.). Specific Heat of Water 1002
Wiebe (H. F.). Expansion of Solid and Liquid Bodies 1002
Amagat (E. H.). Compressibility of Gases at High Pressures . . . 1004
Clarke (F. W.). Some Specific Gravity Determinations 1004
Koch (K. R.). Changes in the Surface of Platinum and Palladium produced by Oxygen-polarisation 1005
Troost (L.). Employment of Diffusion in the Study of the Phenomena of Dissociation 1006
Berthelot. Remarks on a Note on Chloral Hydrate by Wurtz . . . 1006
Ditte (A.). Researches on the Decomposition of Metallic Salts, and on Certain Inverse Reactions which take place in Presence of Water . . 1006

Inorganic Chemistry.

Solvay (E.). Preparation of Chlorine and Hydrochloric Acid by means of Calcium and Magnesium Chlorides 8
Holdermann (E.). On Hydrochloric Acid containing Phosphoric Acid . 8
Jeremin. Ozone 8

PAGE

BERTHELOT. Oxidation of Nitrous Acid by Ozone and by Moist Oxygen . 9
DIEULAFAIT (M. L.). Presence of Ammoniacal Salts in Sea-water . . 9
SNYDERS (A. J. C.). Chemical Action of Water and Saline Solutions on Zinc 11
SMITH (J. L.). A New Earth of the Cerium Group, and on the Analysis of Natural Niobates 12
SMITH (J. L.). The supposed New Element, Mosandrium 12
MARIGNAC (C.). On the Discovery of a New Earth, announced by J. L. Smith 13
LIST (K.). Magnetic Compounds having the formula, $R''O.Fe_2O_3$. . 13
CLERMONT (P. de) and J. FROMMEL. Dissociation of Metallic Sulphides . 13
BÖTTGER (R.). Formation of Hydrogen Peroxide by the Explosion of a Mixture of Oxygen and Hydrogen 103
CORNE (J.). Reduction of Iodates by Phosphorus 103
VULPIUS (G.). Solubility of Sulphur and Phosphorus 104
ETARD (A.). Researches on the Sulphates 104
HENSGEN (C.). Action of Hydrochloric Acid Gas on Sulphates . . . 105
HENSGEN (C.). Action of Hydrochloric Acid on Double Sulphates . . 105
SALZER (T.). Hypophosphoric Acid and its Salts 105
BÖTTGER (R.). Preparation of Salts in a finely-divided State . . . 107
PHILIPP (G. H.). Green and Blue Ultramarine 108
HOFFMANN (R.). Ultramarine 108
MARIGNAC (C.). The Gadolinite Earths 113
DELAFONTAINE (M.). Terbium and its Compounds, and the probable Existence of a New Metal in the Samarskite of N. Carolina . . . 114
DELAFONTAINE (M.). Philippium. 116
DELAFONTAINE (M.). The Mosandrium of J. L. Smith 117
DELAFONTAINE (M.). Decipium, a New Metal from Samarskite . . . 117
MARIGNAC (C.). Ytterbium, a New Metal from Gadolinite 118
DELAFONTAINE (M.). The Probable Compound Nature of the Didymium from Cerite 119
BÖTTGER (R.). Pyrophoric Iron 119
JÖRGENSEN (S. M.). Cobalt-ammonium Compounds 119
KESSEL (F.). Double Salts of Cuprous Thiosulphate 124
MATTHEY (F.). Decomposition of Lead Sulphate by Sodium Chloride . . 124
VULPIUS (G.). Mechanical Purification of Mercury 125
SEUBERT (C.). Atomic Weight of Iridium 125
SEUBERT (C.). Double Salts of Dyad Iridium 125
LUNGE (G.). Preparation of Nitrous Acid 200
PICKERING (S.). Ammonium Nitrate 200
BECKURTS (H.) and R. OTTO. Sulphuric Monochloride and Dichloride . 200
CLAUSNIZER (F.). Action of Sulphuric Monochloride on the Chlorides of Titanium, Antimony, Tin, and Silicon 201
CLAUSNIZER (F.). Sulpho-selenium Oxytetrachloride 201
ERLENMEYER (E.). Studies of the Phosphates 201
FASSBENDER (R.). Double Salts of Calcium Sulphate 203
RICKMANN (R.). Constitution of Ultramarine 203
LEHMANN (A.). Constitution of Ultramarine 204
BROWN (W. G.). Philippium 204
SMITH (J. L.). Remarkable Specimen of Silicon-iron 204
MORAWSKI (T.) and J. STINGL. Potassium Permanganate and its Oxidation Products 204
THOMSEN (J.). Zinc Sulphydrate 206
THOMSEN (J.). Composition of Precipitated Copper Sulphide . . . 206
LÖSECKE (A. v.). Formation of Ammonium Nitrite 298
PICHARD. Alkaline Reaction of Free, Mixed, and Combined Magnesium Carbonates and Silicates 298
SCHULERUD (L.). On Chromates and Dichromates 298
BAUBIGNY (H.). The Oxide of Nickel, Ni_3O_4 299
DITTE (A.). Action of Hydracids on Mercuric Sulphate, and of Sulphuric Acid on the Haloïd Salts of Mercury 299

PAGE

Menke (A. E.). Reactions of Iodine and of Potassium Iodide with Sulphurous Acid 352
Leeds (A. R.). Action of Potassium Permanganate on Oxalic Acid . . 353
Schöne (E.). Hydrogen Peroxide 353
Clausnizer (F.). Experiments on the Preparation of Sulphuric Bromide and Sulphur Oxytetrabromide 354
Vogler (H.). Composition of Commercial Ammonium Carbonate and of the Product formed on exposing it to Air 354
Schneider (R.). Atomic Weight of Antimony 354
Letts (E. A.). Some Bismuth Residues 355
Lefort (J.). Tungstates of the Earthy and Metallic Sesquioxides . . 355
Berthelot. Ozone and the Silent Electric Discharge 435
Ogier. Liquefaction of Silicium Hydride 436
Horstmann (A.). Relative Affinity of Oxygen for Carbonic Oxide and Hydrogen. Part II 436
Bourgeois (L.). Crystalline Barium Chromate 437
Lösekann (G.). Action of Sulphuretted Hydrogen on Alkaline Solutions of Alumina 437
Heumann (R.). Silver Ultramarine 437
Müller (F. C. G.). Gases in Iron and Steel 437
Vortmann (G.). Cobalt-ammonium Compounds 438
Gerresheim (H.). Ammoniacal Mercury Compounds 438
Fluegger (T.). Spitting of Silver 438
Troost (L.). New Compounds of Hydrochloric Acid with Ammonia . . 501
Lunge (G.). Existence of Nitrous Anhydride in the Gaseous State . . 502
Riban (J.). Compounds of Hydrogen Phosphide with Cuprous Chloride, and its Estimation in Gaseous Mixtures 503
Schering (E.). Manufacture of Potassium Iodide 504
Schering (E.). Lead in Potassium Iodide 504
Cros (C.). Action of Light of different Colours on Silver Bromide impregnated with various Organic Colouring Matters 504
Konigel-Weisberg (J.). Action of Chlorine on Barium Hydrate . . 505
Whewell (G.). Analysis of Bleaching Powder 505
Ultramarine 506
Bayley (T.). Complex Oxides of Cobalt and Nickel 507
Sendtner (R.). Some New Salts of Uranyl 507
Brühl (J. W.). Purification of Mercury 508
Emmerling (O.). Metallic Phosphides 508
Schiel (J.). Formation of Ozone by Hydrocarbons 592
Schöne (E.). Hydrogen Peroxide 592
Schöne (E.). Hydrogen Peroxide 592
Guyard (A.). Action of Oxalic Acid on Chlorates, Bromates, and Iodates . 593
Etard (A.). Researches on the Sulphates 593
Guyard (A.). Iodated Potassium Iodide 595
Müller (H.) and C. Pauly. Preparation of Potassium Nitrite . . . 595
Pechiney (A. R.). Preparation of Anhydrous Sodium Sulphate from Glauber Salt 596
Konigel-Weisberg (J.). Action of Chlorine on Strontia 596
Buchner (E. W.). Ultramarine 597
Deniel (W.). Amidonitrosulphide of Iron 597
Jörgensen (S. M.). Cobalt-ammonium Compounds 597
Gorgeu (A.). Artificial Manganese Dioxide 600
Lefort (J.). On Tritungstates 600
Nilson (F. L.). Scandium 601
Nilson (F.). Ytterbia 601
Cleve (P. T.). Chlorostannates of the Rare Earths 601
Meyer (L.). Purification of Mercury 602
Brühl (J. W.). Purification of Mercury 602
Köhler (H.). Mercuric Iodide 602
Clausnizer (F.). Sulpho-oxychlorides 691

PAGE

RAMME (G.). Sulphides of Phosphorus 691
DONATH (J.). Preparation of Barium from Barium-amalgam . . . 691
TERREIL (A.). New Determination of the Equivalent of Aluminium . . 692
HEUMANN (K.). Potassium Ultramarine 692
MOISSAN (H.). Amalgams of Chromium, Iron, Manganese, Nickel, and Cobalt 693
MEUNIER (S.). Artificial Production of Native Carburetted Iron . . . 693
ROSENFELD (M.). Cuprous Chloride 693
MEULEN (B. VAN DER). A New Copper Nitrite 693
RICHE (A.). Action of Light on Silver Chloride 694
SCHAER (E.). Decomposition of the Haloïd Salts of Mercury . . . 694
POTILITZIN (A.). Action of Chlorine on Anhydrous Metallic Bromides . 770
LUNGE (G.). Behaviour of the Nitrogen-acids with Sulphuric Acid . . 770
SMITH (J. L.). Crystals Extracted from Cast Iron by Ether . . . 771
BERTHELOT. Action of Organic Solvents on Sulphur and on Metallic Sulphides 771
POTILITZIN (A.). Action of Selenium on Metallic Sulphides . . . 771
RAMMELSBERG (C.). Behaviour of Silicates containing Fluorine, especially Topaz and Mica, at High Temperatures 772
KRAUT (K.). Mercuric Iodide 772
KESSLER (F.). Atomic Weight of Antimony 772
MATTHEY (G.). Preparation of Iridio-platinum 772
THOMSON (J. S.). Preparation of Distilled Water free from Ammonia . 878
SCHÖNE (E.). Electrolysis of Hydrogen Peroxide 878
ENGEL (R.) and MOITESSIER. Dissociation of Ammonium Sulphide . . 879
ENGEL (R.) and MOITESSIER. Dissociation of Ammonium Hydrosulphide . 879
ENGEL (R.) and MOITESSIER. Dissociation of Ammonium Hydrosulphide . 880
ISAMBERT. Dissociation of Ammonium Hydrosulphide 880
TROOST (L.). Basic Hydrosulphides of Ammonia 880
ST. CLAIRE DEVILLE (H.). Density of the Vapour of Ammonium Dihydrosulphide 880
COQUILLION (J.). Action of Aqueous Vapour on Carbonic Oxide in presence of Red-hot Platinum 880
LEEDS (A. R.). Ammonium Nitrate and the Bye-products obtained in the Ozonisation of Air by Moist Phosphorus 881
MALLET (J. W.). Nitrogen Iodide 882
RAMME (G.). Phosphorus Sulphides 883
BERTHELOT. Chemical Constitution of Amalgams of the Alkali-metals . 883
DEMEL (W.). Zinc and Cadmium Arsenates 884
URBAIN and RENOUL. A Compound of Alumina with Carbonic Acid . . 885
RINNE (A.). Ultramarine 885
BÜCHNER (E. W.). Red and Yellow Ultramarine 885
DEBRAY (H.). Peculiarity of an Experiment of Gay-Lussac and Thénard . 887
MOISSAN (H.). Iron reduced by Hydrogen 887
HENGSEN (C.). New Double Salt of Chromic Acid 887
HAMMERL (H.). Solution of Carbonic Oxide in an Acid Solution of Cuprous Chloride 887
SCHERTEL (A.). Grey Modification of Tin 888
ARNOLD (A. E.). Solubility of Stannic Oxide in Hydrochloric Acid . . 888
SCHIFF (H.). Tungsten Oxychlorides and Chlorides 888
VULPIUS (G.). Formation of Mercuric from Mercurous Chloride . . 889
KÖHLER (H.). Mercuric Iodide 889
JUSSIEU (F. DE). Alloys of Lead and Antimony 889
BOISBAUDRAN (L. DE). Samarium, a new Metal from Samarskite . . 889
DAHLL (T.). Norwegium, a New Metal 890
HIORTDAHL. A New Metal discovered by T. Dahll 890
LIEBEN (A.). Density of Chlorine at High Temperatures . . . 1011
LECHARTIER (G.). Action of Potassium-pyrogallol on Nitric Oxide . . 1012
STINGL (J.) and T. MORAWSKI. Production of Sulphur from Sulphurous Acid and Hydrogen Sulphide 1012

PAGE

FLETCHER (J.). Preparation of Sulphuretted Hydrogen 1013
PFEIFFER (E.). Tetrathionic and Pentathionic Acids 1013
MEYER (V. and C.). Vapour-densities of some Metallic Chlorides . . 1013
RICKMANN (R.). Constitution of Ultramarine 1014
VARENNE (L.). Formation of Crystallised Metallic Oxides by means of Potassium Cyanide 1016
DEMEL (W.). Zinc Phosphates 1016
VARENNE (L.). Compound of Chromic Acid with Potassium Fluoride . . 1016
ALLEN (A. H.). Presence of Nitrogen in Steel 1017
KÖHLER (H.). Mercuric Chloriodide 1017
EDISON (T. A.). Action of Heat on Metals in a Vacuum 1018

Mineralogical Chemistry.

KENNGOTT (A.). The Fundamental Forms of Crystal Species . . . 14
MOORE (G. E.). Hetaerolite, a New Mineral 17
BURGHARDT (C. A.). The Origin of some Ores of Copper 17
REICHARDT (E.). Uranium Pitchblende from Joachimsthal. . . . 18
KENNGOTT (A.). Polydymite 18
ZEPHAROVICH (V. v.). Yellow Dolomite from Bleiberg 19
REICHARDT (E.). A Boron Mineral from Chili 19
GUYOT (P.). Deposits of Calcium Phosphate in the Vosges . . . 19
BRUSH (G. J.) and E. S. DANA. New Minerals from Fairfield Co., Connecticut 20
NORDENSKIÖLD (A. E.). Thaumasite, a New Mineral Species . . . 21
NORDENSKIÖLD (A. E.). Some Minerals from Laangban 21
ZEPHAROVICH (V. v.). Magnetite from Monte Mulatto, S. Tyrol. . . 23
ZEPHAROVICH (V. v.). The Mirabilite from Aussee 23
WICHMANN (A.). The Sericite Rocks of the Taunus 23
BERWERTH (F.). Examination of Lithia-mica from Paris (Maine), Rozena, and Zinnwald 23
BAUER (M.). The Crystal-System of Potash Mica 24
LIEBISCH (T.). Occurrence of Disthene in Central Africa 24
COLLINS (J.). Duporthite, a new Asbestiform Mineral. 24
GÜMBEL (C. W.). The Stone of the "Julius Column," the Lavez Rock in the Upper Engadine, and the Sericite-gneiss in the Bündener Alps . . 25
KALKOWSKY (E.). The Granite-porphyry of Beucha, near Leipzig . . 27
LIEBISCH (T.). Mineralogical-petrographical Notes on the Granite-porphyry of Lower Silesia 29
BURGHARDT (C. A.). Occurrence of Dioptase on Chrysocolla, from Peru . 30
KENNGOTT (A.). On Unghwarite, Nontronite, Gramenite, &c. . . . 31
PAIJKULL (S. R.). Mineralogical Notices 31
DESCLOIZEAUX and DAMOUR. Homilite 32
SMITH (J. L.). Daubréelite, the New Meteoric Mineral 33
MEYER (R.). The Mineral Spring of "Tenninger Bad," Somvixer Tobel, Grisons 33
LUCA (S. DE). Presence of Lithium in the Earth and Water of the Solfatara, at Puzzuoli 33
WROBLEWSKY (E.). Mineral Waters of the Couban, in the Caucasus . . 125
BALLO (M.). Mineral Waters of Buda-Pesth 125
PLANTA-REICHENAU (A. v.). The Mineral Springs of Passugg, Solis, and Tiefenkasten in the Grisons, Switzerland 126
LASAULX (H. v.). Breislakite 206
GÜMBEL (C. W.). Phyllite or Sericite-Gneiss 207
POHL (J. J.). Method of Detecting the Difference between Natural and Artificial Turquoise 209
WARTHA (V.). Preliminary Note on the Analysis of the Zsadány Meteorite 210
GRIMSHAW (H. and C.). Analysis of the Water of Thirlmere . . . 211

PAGE

Vohl (H.). Mineral Spring "Marienbrunnen," near Iserlohn, Westphalia 211
Vohl (H.). Ofner Radóczy-Bitter water 211
Helm (O.). Microscopical Properties of Amber, and the amount of Sulphur contained in it 300
Helm (O.). Gedanite, a new Fossil Resin 300
Hesse (O.). On Asphalte and other Retinalites 301
Thomas (J. W.). Composition of the Gas which issued from one of the Shafts of Abercarn Colliery 357
Rouville (P. de). Natural Crystals of Magnesium Sulphate (Epsomite) of large size 358
Lasaulx (A. v.). Crystal System of Tridymite 358
Ludwig (E.). Milarite 358
Fouqué (F.) and M. Lévy. Production of Felspars by Fusion and by Prolonged Maintenance at a Temperature near that of Fusion . . . 358
St. Meunier. Artificial Crystallisation of Orthose 359
Koch (A.). Adular from Verespatak 359
Lasaulx (A. v.). Saccharite 360
Land (O.). Garnet, from the Erratic Gneiss of Wellen, near Bremen . . 361
Klien. Chromium-Garnet in Silesia 361
Klien. Catlinite 361
Credner (H.). The Red Gneiss of the Saxon Erzgebirge 361
Cossa (A.). Serpentine from Verrayes (Aosta) 362
Liebisch (T.). Some Syenite-porphyries of South-West Norway . . 362
Lasaulx (A. v.). An Intergrowth of two Micas from Middletown, Connecticut 363
Meyer (O.). Twin Zircon Crystals 363
Zepharowich (W. v.). New Mineral Occurrences in the Iron-ore District of Moravicza, in the Banat 363
Nordenskiöld (A. E.). Mineralogical Notes 364
Lasaulx (A. v.). Iodobromite, a New Silver Haloïd 365
Meyer (O.). The Rock of the St. Gotthard Tunnel 366
Buchner and Tschermak. The Meteoric Iron of Hungen 366
Fresenius (R.). Alkaline Constituents of the Hunyadi János Springs at Buda-Pest 366
Baumhauer (H.). "Etch Figures" on Quartz Crystals 439
Klocke (F.). The "Etch Figures" produced on the Alums . . . 439
Streng (A.). Sulphide of Iron and Silver from Andreasberg . . . 440
Bertrand (E.). Cinnabar Crystals from California 440
Pisani (F.). Double Selenides of Lead and Copper 440
Schroeckinger (v.). Dietrichite, a New Alum from Hungary . . . 440
Pisani (F.). Wagnerite, from Bamle, in Norway. Russian Retinite . . 441
Koch (A.). Pseudobrookite and Szaborite, new Minerals 441
Bertrand (E.). The Crystal Form and Twin-formation of Leucophane . 442
Doelter (C.). Diopside 442
Mallard (E.). Bravasite, a New Mineral 442
Knop (W.). Diabase from Berneck 443
Killing (K.), The Gneiss of the North Eastern Schwartzwald, and its Relationship to the Mineral Veins 443
Dieulafait (L.). The Existence of Barium and Strontium in all Rocks constituting the Primary Formation 444
Wigner (G. W.). On Cleopatra's Needle 445
Hiriakoff (M.). Examination of a Meteorite found in the Neighbourhood of Bedjansk 445
Willm (E.). Mineral Waters of Auvergne 446
Cumenge (E.) and E. Fuchs. The state in which the precious Metals exist in certain Minerals, Rocks, and Artificial Products 509
Klien. Fluorite from Evigtok in Greenland 511
Schmidt (A.). A Decomposition of Hornstone 511
Schmidt (A.). Quartz Diorite from Yosemite 512

PAGE

MASKELYNE (N. S.). Artificial Diopside formed in a Bessemer Converter . 513
MASKELYNE (N. S.). Enstatite from South Africa 513
TRIPPKE (P.). The Enstatite in the Olivine Nodules of the Gröditzberg . 514
TRIPPKE (P.). The Twin Formation of Phillipsite from Sirgwitz . . 515
RATH (G. v.). Crystals of Amazonstone (Microline) from Pike's Peak, Colorado 515
TACCHINI (M.). Ferruginous Particles deposited by a Sirocco at certain places in Italy 515
REICHARDT (E.). Analysis of the Water of the Mineral Spring at Suhl . 516
GAUDIN (M. A.). Application of the Author's Atomic Theory to Certain Minerals 602
GUIGNET (E.). Constitution of Coal 602
STILLMAN (J. M.). Bernadinite, a Resinous Mineral from California . . 603
PRECHT (H.). Composition of the Combustible Gases in the Stassfurt Potash Mines 603
KLEIN (P.). Diaspore from Jordansmühl 603
BAUER (M.). The Hydrohæmatite of Neuenberg 604
HANSEL (v.). Phosgenite from Monte Poni, Sardinia 604
TSCHERMAK (G.). Pelagosite 604
KOENIG (G.). Ankerite from Phœnixville 604
KLEIN (P.). Manganosite from Langban, Sweden. 605
LASAULX (A. v.). Optical Properties and Crystal Form of Tridymite . . 605
BRÖGGER (W. C.). Occurrence of Thomsonite at Läven 605
KOENIG (G.). Simultaneous Occurrence of Grossular, Zoisite, Stilbite, and Leidyite 606
RAUFF (H.). Chemical Composition of Nepheline, Cancrinite, and Microsommite 606
KLIPSTEIN (v.). The Nepheline Rock of Meiches in the Odenwald . . 607
SANDBERGER (F.). Occurrence of Tin in Silicates 608
BRÖGGER (W. C.). The Crystal System of Mosandrite. 608
KALKOWSKY (E.). The Leucitophyr of Lake Averno 609
MEUNIER (S.). Metallic Granules of Sporadosidereal Meteorites . . . 609
COHEN (E.). The Meteorite of Zsadány, Temesvar 609
DAUBRÉE. A Meteorite belonging to the Eukrite Group 610
MAURO (F.). The Spinelle of Tiriolo in Calabria 694
PENFIELD (S. L.) Chemical Composition of Triphylite 695
COSSA (A.). Distribution of Cerium, Lanthanum, and Didymium . . 695
ADAMS (F. D.). Presence of Chlorine in Scapolites 697
WILLM (E.). Presence of Mercury in the Mineral Waters of Saint-Nectaire 697
PATERNÓ (E.) and G. MAZZARA. Thermal Water of Termini Imerese . . 698
PORVER (F. B.). Mineral Water of Rosheim in Alsace 698
BALLAND. Waters of the Chéliff 699
BRUSH (G. J.) and E. S. DANA. A new and remarkable Mineral Locality in Fairfield Co., Connecticut, U.S.A. 891
SMITH (J. L.). The Native Iron of Greenland, and the Dolerite which incloses it 892
HELM (O.). The Sulphur in Fossil Resin 896
RUSSELL (J. C.). Occurrence of a Solid Hydrocarbon in the Eruptive Rocks of New Jersey, U.S.A. 896
FREMY (E.). Artificial Formation of Coal 896
SCHRAUF (A.). The Tellurium Ores of Siebenbürgen 897
STRENG (A.). Sulphide of Silver from Andreasberg 898
ARZRUNI (A.). Crystallographical and Chemical Examination of some Arsenical Pyrites 900
CARNOT (A.). Mallardite, a New Natural Manganese Sulphate; and Luckite, a New Variety of Iron Sulphate 901
SCHUMACHER (E.). Growth-phenomena on Quartz Crystals from Krummindorf, near Strehlen 901
WEISBACH (A.). Cacochlor from Rengersdorf, near Görlitz . . . 901

PAGE

SCHUMACHER (E.). Idocrase in the Limestone Strata of Deutsch-Tschammendorf 902
SCHUMACHER (E.). Granular Plagioclase in the Limestone Strata of Gepersdorf 902
HARTMANN (M.). Basalts of the Auckland Islands 903
COSSA (A.). Cinder and Lava from Etna 904
Report on the Researches of S. Meunier relative to Meteoric Nickeliferous Iron and the Native Iron of Greenland 905
D'ABBADIE. Amount of Nitric Acid in the Waters of the Nile 905
JOHNSTONE (W.). Analysis of the Water of St. Dunstan's Well, Melrose . 905
PHIPSON (T. L.). Water from the River Dart 906
ESTCOURT (C.). Analyses of the Waters of Lake Thirlmere and the River Vyrnyw 906
DIEULAFAIT (L.). Distribution of Copper in Primordial Rocks, and in the Sedimentary Deposits derived from them 1020
MACADAM (W. J.). Composition of a Nodule of Ozokerite found at Kinghornness 1020
SCHWARZ (H.). Composition of Pyropissite 1021
MALLET (J. W.). Barcenite, a New Antimonate from Huitzuco, Mexico . 1022
RŒPPER (W. T.). On a Pseudomorph after Anorthite, from Franklin, New Jersey 1023
MAUMENÉ (E.). Composition of Slate 1024
DAUBRÉE (A.). Experiments on the Erosive Action of Strongly Compressed Hot Gases, with Reference to the History of Meteorites . . . 1024
ANDREWS (T.). Curious Concretion-balls derived from a Colliery Mineral Water 1024

Organic Chemistry.

ELTEKOFF. Reactions of the Halogen Compounds of the Olefines . 34
HENRY (L.). A New Unsaturated Sexvalent Hydrocarbon, Diallylene, C_6H_8 34
TÖNNIES (P.). Action of Nitrous Acid on Unsaturated Hydrocarbons. . 35
CLARKE (J. W.). Some Seleniocyanates 35
RABUTEAU (L.). Alcohols in Potato Fusel-oil 36
MENSCHUTKIN (N.). Etherification of Primary Alcohols 36
FLAWITZKY. Amyl Compounds 37
BECKMANN (E. O.). Oxidation Products of Diethyl Sulphide and Analogous Compounds 37
LIEBERMANN (C.) and O. HÖRMANN. Glucoside of Buckthorn Berries and Rhamnodulcite 39
BEREND (L.). Isodulcite 40
SCHMIDT (E.). "Mercurialine" (Methylamine) 40
RUDNEFF (W.). Trimethylcarbamine 40
RATHKE (B.). Sulphuretted Dicyanodiamine 41
PINNER (A.) and F. KLEIN Butyl Chloral Hydrocyanide 41
WALLACH (O.). Chloralide and its Derivatives 43
KRÄMER (C.). and M. GRODZKI. The Acids of Wood-vinegar and their connection with the so-called Wood-oils 43
MILLER (W. v.). Angelic Acids of Different Origin 45
BÖTTINGER (C.). Monosulpholactic Acid 45
BÖTTINGER (C.). Action of Phosphorus Pentasulphide on Organic Acids . 45
CLAISEN (L.) and J. SHADWELL. Synthesis of Pyroracemic Acid . . 45
RASCHIRSKY (M.). Action of Zinc-methyl on the Bromides of Monobrominated Acid Radicles of the α-Series 46
PINNER (A.) and F. KLEIN. Conversion of Nitrils into Imides . . . 46
RUDNEFF (W.). Action of Iodine on Thiocarbamides 48
MABERY (C. J.) and H. B. HILL. Dimethyluric Acid 48
LE BEL and GREENE. Action of Zinc Chloride on Methyl Alcohol; Hexmethylbenzene 49

PAGE

Austen (P. T.). On Dinitroparadibromobenzenes and their Derivatives . 50
Hepp (E.). Some Addition-products of Trinitrobenzene and other Nitro-compounds 50
Böttinger (C.). Action of Aniline on Glyoxylic Acid 51
Schaumann (W.). Paraxylidine 51
Iles (M. W.) and I. Remsen. Oxidation of Sulphamidoxylene . . . 52
Jacobsen (O.). Oxidation of Metaxylenesulphamide 53
Fischer (O.). Condensation-products of Tertiary Aromatic Bases . . 53
Landgrebe (O.). Cyanoguanidine 53
Heintz (W.). Benzaldiacetonamine 54
Rathke (B.). Phenylthiocarbamic Acid 54
Benedikt (R.). Pentabromoresorcin 55
Schreder (J.). Fluoresceïn-carbonic Acid 55
Benedikt (R.). Trinitroso- and Trinitro-phloroglucin. 57
Dale (R. S.) and C. Schorlemmer. Aurin 58
Zulkowsky (C.). Aurin 58
Caro (H.) and C. Graebe. Rosolic Acids 59
Buchka (K.). Reduction of Acetophenone 61
Engler (C.). A Sulphuretted Derivative of Acetophenone . . . 61
Engler (C.). Sulphuretted Derivatives of Benzophenone 61
Jacobsen (O.) and E. Weinberg. Dibromo-metaxylene-sulphonic Acid . 61
Landgrebe (O.). Oxidation of Ditolylparabanic Acid . . . 62
Jackson (C. L.) and A. W. Field. Parachlorobenzoyl Chloride and Bromide 62
Sommaruga (E. v.). Vapour-density of Indigo 63
Sommaruga (E. v.). Action of Ammonia on Isatin, II 63
Barth (L.) and J. Schreder. Diphenol 64
Losanitch (S. M.). Action of Potash on Tetranitrodiphenyl-carbamide . 67
Kelbe (W.). Naphthyl-phosphorus and Naphthyl-arsenic Compounds . 67
Schunck (E.) and H. Roemer. Metabenzdioxyanthraquinone . . . 68
Engler (C.). Tetraphenylethane 68
Wreden (F.). Camphor 69
Ciamician (G.). Reduction-products of Elemi-resin with Zinc-dust . . 69
Luca (S. de). Splitting up of Cyclamin into Glucose and Mannite . . 70
Nencki (M.). and N. Sieber. New Synthesis of Glycocyamine . . . 70
Action of Iodic Acid, "Sulphomolybdic Acid," and Ferric Chloride on Morphine and other Substances 70
Hesse (O.). Remarks on Rice's Articles on the Cinchona Alkaloïds . . 71
Hesse (O.). Substitutes for Quinine 71
Skraup (Z. H.). Cinchonine and Cinchonidine 71
Hesse (O.). Remarks on Cinchonine and Cinchonidine . . . 71
Schreiner (P.). A New Organic Base in the Animal Organism . . . 72
Hesse (O.). Lotur Bark 73
Hesse (O.). Amyrin and Icacin 73
Boussingault. Composition of the Milk of the Cow-tree 73
Long (H.). Action of Alcoholic Potash on Bromoform 126
Preparation of Ethyl Bromide 127
Reboul. Isomerism in the Propyl Series 127
Flavitzky (F.) and P. Kriloff. Isopropylacetylene 134
Walitzky (W.). Derivatives of Brain Cholesterin 135
Latschinoff (P.). Some Neutral Oxidation-products of Cholesterin . . 135
Witt (O.). Presence of Ethyl Alcohol in Coal-tar 136
Saytzeff (A. and P.). Preparation of Dipropylallyl Carbinol . . . 136
Flavitzky (F.). Dehydration of Propylene-glycol 136
Tollens (B.). Specific Rotatory Power of Cane Sugar 136
Foudlakowsky (G.). Lactoglucose and Galactose 137
Meyer (V.). Occurrence of Furfuraldehyde in Glacial Acetic Acid . . 137
Köhler (H.). Decomposition of Ethyl Sulphates by Gaseous Hydrochloric Acid 137
Köhler (H.). Action of Ammonium Sulphate on Barium Ethylsulphate . 137

PAGE

Kessel (F.). Bromo-derivatives of Ethyl Acetate 137
Böttinger (C.). Thioglycollic and Thiodiglycollic Ethers 138
Richter (V. v.). Action of Phosphorus Pentachloride on Ethyl Oxalate . 138
Meyer (R.). Hydroxylation by Direct Oxidation 139
Schmidt (E.) and R. Sachtleben. Isobutylformic Acid (Inactive Valeric Acid) 139
Hecht (O.) and J. Munier. Isoheptylic Acid from β-Hexyl Iodide . . 140
Heinzelmann (R.). Dehydromucic Acid 141
Rudneff (W.). Trimethylcarbamine 141
Böttinger (C.). Acetylene-carbamides 142
Fittig (R.). Uric Acid Formula 142
Körner (H.). Paradipropylbenzene and its Derivatives 142
Gustavson (G.). Bromination of Aromatic Hydrocarbons in presence of Aluminium Bromide 142
Beilstein (F.) and A. Kurbatow. Chloranilines 143
Beilstein (F.) and A. Kurbatow. Formation of Chlorophenylene-diamine 144
Malachite-green 144
Heintz (W.). Vanillo-diacetonamine 144
Bernthsen (A.) and H. Trompetter. Amidines and Thiamides of Monobasic Organic Acids 146
Pinner (A.) and F. Klein. Imido-thio-ethers 147
Goldstein (M.). Action of Nitric Acid on Phenol and on Nitrophenol . 148
Goldstein (M.). Dibenzoyl-dinitro-diphenol 148
Caro (H.) and Schraube. Phenoldiazobenzene 148
Baumann (E.). Hydrogen-Phenyl Sulphate and similar Derivatives of the Phenols 148
Golubeff. Action of Nitric Acid on Deoxybenzoïn 150
Ittica (F.). Nitrobenzoic Acids 150
Widnmann (E.). Isomeric Nitro- and Amido-benzoic Acids and Formation of Chloranil from the latter 154
Cöllen (T.). Sulphoparachlorobenzoic Acid 155
Schmitz (H. J.). Substitution Products of Mesitylenic Acid . . . 155
Schiff (R.). Synthesis of Metanitrocinnamic Acid 157
Meyer (R.) and J. Rosicki. Oxypropylbenzoic Acid 157
Barth (L.). Dioxybenzoic Acid 157
Barth (L.). Thymoloxycuminic Acid. 158
Fittig (R.) and W. F. Hillebrand. Quinic Acid 159
Etti (C.). Malabar-kino and Kinoïn 159
Johanson (E.). Chemical Constituents of the Willow and its Pathological Formations; certain Reactions with Tannins and Allied Substances . 160
La Coste (W.) and A. Michaelis. Mono- and Di-phenyl Compounds of Arsenic 161
La Coste (W.) and A. Michaelis. Triphenylarsine and its Derivatives . 162
La Coste (W.) and A. Michaelis. Monotolyl Compounds of Arsenic . 163
Schmidt (H.) and G. Schultz. Diphenylbenzenes 163
Fittig (R.) and A. Schmitz. Diphenylene-methane 164
Schmitz (A.). Diphenylene Ketone and Phenylbenzoic Acid . . . 164
Hummel (J.). Diphenic Acid 165
Meldola (R.). Naphthalene-derivatives 165
Fittig (R.) and F. Gebhard. Fluoranthene, a new Hydrocarbon from Coal-tar 165
Goldschmidt (G.). Idrialin 167
Flavitzky (F.). Structure of Terpenes 167
Flavitzky (F.). Dextro-gyrate Terpene from the Turpentine of *Pinus sylvestris* 168
Spitzer (F. V.). Camphene from Camphor, and its Homologues. . . 168
Spitzer (F. V.). Camphor Dichloride 168
Claus (A.). Cinchona Alkaloïds 168
Drygin. A New Quinine Salt 169

PAGE

DRYGIN. Cinchonichine, a New Cinchona Alkaloïd 169
DURAND. Bark of the Root of the Pomegranate 169
TANRET (C.). Pelletierine, a Base from the Bark of the Pomegranate . . 170
DISQUÉ (L.). Urobilin 170
HOLDERMANN (E.). Iron Albuminates 170
BÖTTGER (R.). Crystalline Structure of Bees'-wax 171
KUHNEMANN (G.). Constituents of Hops 171
ERDMANN (J.). Colouring Matter of Red Wine 171
STAEDEL (W.). Halogen-derivatives of Ethane and Ethylene 212
SAYTZEFF (A.) and SCHISOKOFF. Diethyl-allyl Carbinol 214
SAYTZEFF (A. and P.) and A. NIKOLSKY. Action of Sulphuric Acid on Allyldimethylethyl- and Allyldipropyl-carbinol 214
MENSCHUTKIN (N.). Etherification of Secondary Alcohols 214
MENSCHUTKIN (N.). Etherification of Tertiary Alcohols and Phenols . . 215
THOMSEN (L.). Action of Potassium Cyanate on Epichlorhydrin . . . 217
RODEWALD (H.) and R. TOLLENS. Reduction of Cupric Oxide by Milk Sugar 217
WOLFRAM (G.). Nitro-componnds of Cellulose 218
PAULEY (C.) and R. OTTO. Decomposition of Ethyl Disulphoxide by Potash 219
KÖHLER (H.). Formation of Ethylamine 219
HOFMANN (A. W.). Formation of Methyl Aldehyde 219
GEUTHER (A.). Diethylglyoxylic Ether and Diethylglyoxylamide . . 220
DEMOLE (E.). Formation of a Ketone containing four Carbon Atoms from Dibromethylene 220
KESSEL (F.). Decomposition of Ethyl Monobrom- and Dibrom-acetate . 220
ZORN (W.). Diazo-compounds of the Fatty Series 221
SCHMITT (E.). The Volatile Acid of Croton Oil 221
ANSCHÜTZ (R.). Action of Ethyl Iodide on the Silver Salts of Malcic and Fumaric Acids 223
STAEDEL (W.). Racemic Acid 223
JACKSON (O. R.) and H. B. HILL. Mucobromic Acid 224
DITTRICH (E.). Methyltaurine, Methyltaurocyamine, and Taurocyamine . 225
PONOMAREFF (J.). Allantoxanic Acid 226
PONOMAREFF (J.). Some Derivatives of Allantoïn 228
ADOR (E.) and A. RILLIET. Hydrocarbons obtained by the Action of Aluminium Chloride on Methyl Chloride and Benzene 228
JACOBSEN (O.). Constitution of the Propyl Group in Cymene . . . 228
BECKURTS (H.) and R. OTTO. Mode of Action of Sulphuric Hydroxychloride 229
GERICHTEN (E. v.). β-Chlorocymene from Thymol 230
BEILSTEIN (F.) and A. KURBATOW. Action of Hydrogen Sulphide on certain Nitro-compounds 230
KLEIN (O.). Compounds of Organic Bases with Mercuric Chloride . . 231
LADENBURG (A.). Experimental Determination of Position 232
LADENBURG (A.). Simple Method for preparing Aldehydines . . . 233
LADENBURG (A.) and L. RÜGHEIMER. The Aldehydines 233
LADENBURG (A.) and T. ENGELBRECHT. Some Phenylaldehydines . . 234
GOLDSCHMIDT (A.). The Three Isomeric Tolidines 235
FISCHER (E. and O.) Certain Colouring Matters of the Rosaniline Group . 236
BARSYLOWSKY. Azo-derivatives of Toluene 237
BANTLIN (A.). Metanitrophenol and its Derivatives 237
STAEDEL (W.) and G. DAMM. Bromonitro- and Bromamido-anisoïl . . 239
PRUNIER (L.). Quercite 239
STAEDEL (W.) and E. SAUER. Dinitrobenzophenone 242
BECKURTS (H.) and R. OTTO. Synthesis of Aromatic Sulphones . . . 242
OTTO (R.) and A. KNOTT. Action of Sulphuric Hydroxychloride on Sulphobenzide 243
PAULY (C.) and R. OTTO. Disulphoxides of Benzene and Toluene . . 243
ANNAHEIM (J.). Tetranitro-oxysulphobenzide 244
JANNASCH (P.) and C. RUMP. Discovery of Vanillin in Siam Benzoin . . 245

PAGE

GABRIEL (S.) and A. MICHAEL. Action of Dehydrating Substances on Anhydrides 245
GRIESS (P.) Derivatives of Benzoic Acid 246
JACOBSEN (O.) Constitution of Oxymesitylenic Acid 248
JAHN (H.). Valonia and certain other Sources of Tannin 248
REMSEN (I.). Oxidation of Xylene-sulphamides 248
ARONHEIM (B.). Synthesis of the Compounds of Phenol with Tin . . 249
DIEHL (T.) and V. MERZ. Naphthopicric Acid and some of its Derivatives . 250
STAEDEL (W.) and KLEINSCHMIDT. Iso-indol 252
SCHMIDT (H.) and G. SCHULTZ. Diphenyl-bases 252
EWALD (H.). Some Coerulignone Derivatives 253
GRÄTZEL (A.). Eupittone and Pittacal 253
PERGER (V.). Derivatives of Anthraquinone 253
LIEBERMANN (C.) and K. BOECK. Anthracene-disulphonic Acid and its Conversion into Anthrarufin 257
GRAEBE (C.). Alizarin Blue. 259
LIEBERMANN (C.). Synthesis of Anthrarufin and Chrysazin from Anthracene 260
KESSEL (F.). Wax of *Ficus gummiflua* 261
HIRSCH (B.). Investigation of *Balsamum antarthriticum indicum* . . 262
RAMSAY (W.). On Picoline and its Derivatives 262
MEYER (A.). Absorption-spectra of Solutions of Brucine, Morphine, Strychnine, Veratrine, and Santonin in Concentrated Acids . . . 269
HESSE (O). Further Remarks on *Alstonia constricta* 269
BLUMBERG (T.). Contribution to a Knowledge of Alkaloïds of Ergot . 269
PICCARD (J.). Cantharic Acid and a Hydrocarbon, C_8H_{12} 270
LIEBERMANN (C.) and O. HÖRMANN. Formulæ of Rhamnetin and Xanthorhamnin 271
BARBIERI (J.). Albuminoïds of Gourd Seeds 272
COQUILLON (J.). Action of Platinum Wire on Hydrocarbons . . . 302
MERZ (V.) and W. WEITH. Action of Bromine on the Lower Paraffins . 302
MERZ (V.) and W. WEITH. Action of Bromine on the Higher Paraffins . 302
MULDER (E.) and G. J. W. BREMER. Action of Chlorine Monoxide on Ethylene 303
DESCAMPS (A.). Potassium Cobaltocyanide 303
MEYER (G.). Action of Carbonic Anhydride on certain Cyanides . . 303
SCHMITT (R.) and O. MITTENZWEY. Action of Diazo-compounds on Ethyl Mercaptan 304
BLEUNARD (A.). Action of Trimethylamine on Carbon Bisulphide . . 305
DUVILLIER (E.) and A. BUISINE. Separation of Ethylamines . . . 306
KELLY (O. J.). Action of Chlorocarbonic Ether on Halogen Compounds of the Fatty Acid Series 306
NENCKI (M.) and F. SCHAFFER. Action of Chloral Hydrate on Ammonium Thiocyanate 306
JAGI. Pæonia Moutân. 306
KRAFFT (F.). Conversion of Undecylenic Acid into Undecylic Acid . 306
TASSINARI (G.). Derivatives of Arachidic Acid 307
MILLER (W. v.). Dimethylacrylic Acid 307
OST (H.). Pyromeconic Acid 307
SCHIFF (R.) and G. TASSINARI. Two Monobromopyromucic Acids . . 308
GUSTAVSON (H.). Compounds of Aluminium Chloride with Benzene and Toluene 308
PATERNÒ (E.). Constitution of Cumic Compounds and of Cymene . . 308
PRUNIER (L.) and R. DAVID. Crystalline-products obtained from Pennsylvanian Petroleum 309
ZORN (W.). Action of Nitrosyl-silver 309
BEILSTEIN (F.) and A. KURBATOW. Chloronitranilines 309
MONNET (P.), F. REVERDIN, and E. NÖLTING. Methylated Derivatives of Aniline and Toluidine, and the Colours obtained therefrom . . . 310
FRIEDERICI (T.). Action of Hydrogen on Metanitro-paratrichloraceto-toluide and Metanitro-paravaleryl-toluide 311

PAGE

Doebner (O.). Malachite Green 312
Magatti (G.). Action of Sulphuric Anhydride on Phenyl-thiocarbimide . 312
Wallach (O.). Organic Thio-compounds 312
Schmitt (R.). Preparation of Azobenzene from Aniline 313
Koenigs (W.). Action of Fuming Nitric Acid and of Nitrous Acid on Benzene-sulphinic Acid 314
Bendix (J.). Derivatives of Ortho-nitrophenol 314
Paternò (E.) and G. Mazzara. Benzylated Cresol 314
Hirsch (R.). The so-called Dichlorazophenol 315
Griess (P.). Action of some Diazosulphonic Acids on Phenols . . . 315
Schmitt (R.) and R. Mohlaü. Azoxy- Azo- and Hydrazo-phenetols . . 317
Thörner (W.) and T. Zincke. Pinacones and Pinacolines. Part IV . 317
Dennstedt (M.). Benzyl Orthothioformate 318
Staedel (W.). Benzophenone 318
Praetorius (H.). Nitration of Benzophenone, Benzhydrol, and Diphenylmethane 319
Doebner (O.) and W. Stackmann. Synthesis of Oxyketones by introducing Acid Radicles into Phenols. Part II 319
Martin (G.). A Japanese Cinnamon Bark 320
Etard (A.). Oxidation of Aromatic Compounds. 320
Paternò (E.). Propylbenzoic Acid 321
Griess (P.). Action of Cyanogen on Amidobenzoic and Anthranilic Acids in Aqueous Solutions 321
Schiff (R.). Metanitrocinnamic Acid 321
Stöckenius (O.). Phenylamidacetic Acid 322
Thörner (W.) and T. Zincke. Diphenylmethylacetic Acid. 322
Fritzsche (P.). Oxyphenylacetic Acid 322
Claisen (L.) and F. H. Morley. New Method of preparing Phenylglyoxylic Acid 322
Gerichten (E. v.) and W. Rössler. α-Oxyparatoluic acid 323
Gabriel (S.). Substituted Phthalanils 323
Friederici (T.). New Method of Preparing Chrysanisic Acid . . . 324
Beck (C.). Dioxydiphenylmethane 324
Gail (F.). Oxidation of Dioxydiphenylmethane 325
Fischer (E. and O.). Triphenylmethane 326
Liebermann (C.) and P. Seidler. Chrysarobin in "Goa Powder" . . 326
Breuer (A.) and T. Zincke. Derivatives of the Hydrocarbon, $C_{16}H_{12}$, from Phenyl Glycol 327
Montgolfier (J. de). Derivatives of Terebenthene 328
Haller (A.). Iodocamphor. 329
Haller (A.). Cyano-derivatives of Camphor 329
Forcrand. Organic Ultramarines 329
Katzujama. Investigation of the Seeds of *Camellia japonica* . . . 330
Martin (G.). Constituents of *Ligustrum Ibotu* 330
Cannizzaro (S.) and Carnelutti. Two Isomerides of Santonin. . . 330
Cannizzaro (S.) and L. Valente. Santonin Derivatives 331
Hesse (O.). Cinchotenicine 332
Hesse (O.). Alstonia Bark 332
Harnack (E.). The Basic Constituent of Dita Bark 332
Martin (G.). *Scopotia japonica* 333
Martin (G.). *Evodia glauca* 333
Destrem (A.). Cholic Acid 333
Fredericq (L.). Hæmocyanin from the Blood of the *Octopus vulgaris* . 333
Staedel (W.). Halogen Derivatives of Ethane 368
Denzel (J.). Nomenclature and Boiling Points of the Chlorobromo-substitution-products of Ethane and Ethylene 368
Reboul. Ethylidene Chlorobromide 369
Le Bel (J. A.). Dextrogyrate Amyl Alcohol 369
Durin. Inversion of Cane-sugar, and Consecutive Alteration of the Glucoses so formed 369

PAGE

Musculus (F.) and J. De Mering. Action of Diastase, Saliva, and Pancreatic Juice on Starch and Glycogen 370
Wolfram (G.). Nitro-derivatives of Cellulose 371
Reboul. Diallyl-acetic Acid 372
Petri (C.). Fumaric and Maleic Acids 372
Meyer (E. v.). Some New Platinum Compounds: Fulminoplatinums. . 373
Grimaux (E.). Synthesis of Uric Acid Derivatives: Alloxan, Uramil, Murexide, &c. 375
Berthelot. Hydrogenation of Benzene and Aromatic Compounds . . 376
Beilstein and Kourbatoff. Dinitrochlorobenzene 376
Fittig (R.). Formation of Unsaturated Hydrocarbons from the Addition-products of Non-saturated Acids 376
Destrem (A.). Compounds of Metallic Salts with Compound Ammonias . 376
Valitsky. Action of Aniline, Toluidine, and Naphthylamine on Cholesteryl Chloride 376
Maillot (E.). Aniline-derivatives of Sebacic Acid 376
Grothe (A.). Metaiodonitro- and Metaiodamido-benzoic Acids . . . 377
Posen (E.). Amidohydro-cinnamic Acid (Phenylamido-propionic Acid) . 378
Fittig (R.) and F. Binder. Addition-products of Cinnamic Acid . . 378
Fittig (R.) and C. Wurster. Atropic and Isatropic Acids . . . 379
Hübner (H.). Nitrosalicylic Acids and the Isomerism of Benzene Derivatives 380
Stahlschmidt (C.). Polyporic Acid 382
Girard and Pabst. Nitrosyl-derivatives 383
Rosenstiehl (A.). Anthraflavone and Anthraxanthic Acid. 383
Fischer (E. and O.). Triphenylmethane and Rosaniline 384
Tilden (W. A.). An Examination of Distilled Essence of Lemon . . 386
Gal (H.) and A. Etard. Researches on Strychnine 387
Blumberg (T.). Contribution to a Knowledge of the Alkaloïds of Ergot . 387
Tappeiner (H.). Action of Potassium Dichromate and Sulphuric Acid on Cholic Acid 388
Kohn (S.). Decomposition-products of Albuminoïds 389
Loew (O.). Oxidation of Albumin by the Oxygen of the Air . . . 389
Ritthausen (H.). Albuminoïds from Castor Oil Seeds 390
Jones (H. W.). Amount of Ash and Soluble Matter in three kinds of Buchu 391
Pebal (L.). Action of Hypochlorous Acid on Ethylene 446
Prunier (L.). Hydrocarbons from American Petroleum 447
Lippmann (E.) and J. Hawliczek. Eikosylene, a Derivative of Lignite Paraffin 447
Saytzeff (A.). Action of Dilute Sulphuric Acid on Allyldimethylcarbinol 447
Schirokoff and A. Saytzeff. Allyldiethylcarbinol 448
Berthelot. Influence of Metallic Chlorides on Etherification . . . 449
Hörmann (J. v.). Action of Hydrocyanic Acid on Epichlorhydrin . . 449
Hanriot. On Glycide 449
Hönig (M.) and M. Rosenfeld. Sugars 449
Villiers (A.). Analysis of Honey from Ethiopia 450
Fischer (E.). Hydrazine-compounds of the Paraffin Series . . . 450
Böttinger (C.). Conversion of Aldehyde into Mercaptan 451
Schiff (R.). Action of Aldehydes on Chloral-ammonia 452
Franchimont (N.). Zinc Acetate 452
Aronheim (B.). On Schützenberger's Chlorine and Iodine Acetates . . 452
Conrad (M.) Identity of Isopropionic Acid and Lævulinic Acid . . 453
Deutsch (A.). Ethereal Salts of Tribasic Formic Acid 453
Wallach (O.) and O. Bischof. Decomposition of Dichloracrylic Acid by Alkalis 453
Kopp (H.). Acids obtained by the Saponification of Roman Chamomile-oil 454
Köbig (J.). Constituents of Roman Chamomile-oil 454

PAGE

PAGENSTECHER (A.). Angelic and Tiglic Acids 455
FITTIG (R.). Constitution of Tiglic and Angelic Acids 456
BOURGOIN (E.). Bromocitraconic Acid 457
DEMARÇAY (E.). Tetric Acid and its Homologues 457
DEMARÇAY (E.). Homologues of Oxyheptic Acid 458
DEMARÇAY (E.). Relations of Tetric and Oxytetric Acids and their Homologues to Succinyl, Malyl, and other Radicles of the Bibasic Acids . 459
GRIMAUX (E.). Synthesis of Uric Acid Derivatives 460
PONOMAREFF (J.). Compounds of the Uric Acid Group 461
GUSTAVSON (G.). Compounds of Aluminium Chloride with Benzene and Toluene 461
LIPPMANN (E.) and G. VORTMANN. Compounds of Cobalt and Nickel Chlorides with Anilines 461
BECCHI (G. v.). Succinyl-compounds of Toluidine 461
LIPPMANN (E.) and W. STRECKER. Amylidene-aniline 462
KRAUSE (A.). Paraphenylenediamine 462
WEITH (W.). Synthesis of Carbotriphenyltriamine 462
ROSENSTIEHL (A.). Constitution of the Rosanilines 463
BEILSTEIN (F.). Perchlorophenol Chloride 463
LIPPMANN (E.) and W. STRECKER. Nitrocuminol and its Derivatives . . 464
NIETZKI (R.). Derivatives of Quinol (Hydroquinone) 464
BENEDIKT (R.). Pentabromoresorcinol 464
ARONHEIM (B.). Action of Nitrous Acid on Resorcinol Ethers . . . 465
SALKOWSKI (E. and H.). Formation of Hydrocinnamic Acid by means of Pancreas Ferment 465
MEYER (R.) and J. ROSICKI. Hydroxypropylbenzoic Acid 465
GRIESS (P.). Amidobenzoic Percyanide 466
SCHIFF (H.). Digallic Acid 466
GUYARD (A.). Laurent's "Carminaphtha" 466
KELBE (W.). Hydrocarbon from Rosin-oil 467
SCHULZE (E.) and J. BARBIERI. Lupinin, a New Glucoside 467
HOFFMANN (E.). Naringin 468
FRANCHIMONT (N.) and WIGMAN. Lactucone 468
FRANCHIMONT (N.) and WIGMAN. Betulin 469
STÜNKEL (C.). Daphnetin 469
HARZ (C. O.). Spergulin, a New Fluorescent Body 469
FRANCHIMONT (N.) and SICHERER. The Colouring-matter of Sandal and Caliatour Woods 470
FRAUDE (G.). Aspidospermine 470
WEYL (T.). Creatinine and Creatine 471
KRAUSE (H.) and G. SALOMON. Formation of Xanthine Derivatives from Albumin 471
KÖNIGS (W.). Oxidation-products of Cinchonine 471
HAMMARSTEN (O.). Paraglobulin 472
TÖNNIES (P.). Action of Nitrosyl Chloride on Unsaturated Hydrocarbons 517
HERZIG (J.). Two New Isomerides of Cyanuric Acid 517
MUSCULUS (F.). Modifications of the Physical Properties of Starch . . 518
HIORTDAHL (M.). Crystalline Form of the Stannmethyl Compounds and their Homologues 518
URECH (F.). Action of Potassium Carbonate on Isobutylaldehyde . . . 520
BRÜHL (J. W.). Preparation of Divaleryl 520
BARDY (C.) and L. BORDET. Preparation of Methyl Formate and Pure Methyl Alcohol 520
KAHLBAUM (G. W. A.). Physical Properties of some Methyl Compounds of 3- and 4-Carbon Acids 521
HELL (C.) and P. SCHOOP. Dibromocapric Acid 521
WERIGO and MELIKOFF. Monochlorolactic Acid and Dichloropropionic Acid from Glyceric Acid 521
BÖTTINGER (C.). The Amount of Water contained in Crystallised Calcium Glycollate 522

PAGE

Schreiner (L.). Boiling points of the Ethereal Salts of Hydroxy- and Alkyloxy-Acids 522
Duvillier (E.). Derivatives of Normal Methoxybutyric Acid . . . 523
Tollens (B.). Oxidation of Levulinic Acid 523
Bandrowski (F.). Reaction of Dibromosuccinic Acid with Water . . 524
Böttinger (C.). Pyroracemic Acid 524
Bell (C. A.) and E. Lapper. Dry Distillation of Ammonium Salts of Saccharic Acid 524
Bell (C. A.). Pyrrol Derivatives 525
Wroblevsky (E.). Structural Formula of Aromatic Compounds . . 526
Ador (E.) and A. Rilliet. Hydrocarbons produced by the Action of Methyl Chloride on Benzene in presence of Aluminium Chloride . . 527
Bechi (G. v.). Succinyl Compounds of the Toluidines 527
Michaelis (A.) and F. Dittler. Reactions of Phenylphosphine . . 528
Salkowski (H.). Behaviour of Metanitranisoïl towards Ammonia . . 528
Bechi (G. v.). New Mode of Formation of Ketones 529
Jacobsen (O.). Products of the Action of Fused Potash on Potassium Mesitylene-sulphonate 529
Sommaruga (E. v.). Molecular Weight of Indigo 532
Schunck (E.). Indigo-blue 532
Claisen (L.) and J. Shadwell. Synthesis of Isatin 534
Baeyer (A.). Action of Phosphorus Pentachloride on Isatin and Allied Compounds 535
Pawlow (D.). Tetramethylethylene and its Derivatives 536
Fittig (R.) and H. Lippmann. Constitution of Isodiphenic Acid and Fluoranthene 536
Smith (W.). Vapour-densities of the three Isomeric Dinaphthyls . . 537
Liebermann (C.). Reduction of Anthraquinone-sulphonic Acids . . 537
Liebermann (C.). Anthracene Derivatives of the Chrysazin Series . . 537
Schultz (G.). Constitution of Phenanthrene 538
Anschütz (R.) and G. Schultz. Phenanthrenequinone 538
Ballo (M.). Action of Dehydrating Agents on Camphoric and Camphoramic Acids 539
Koenigs (W.). Synthesis of Chinoline from Allylaniline 540
Koenigs (W.). Nitrochinoline 540
Weyl (T.). Decomposition of Tyrosine by Putrefaction 541
Hoogewerff (S.) and W. A. v. Dorp. Oxidation of Quinine by Potassium Permanganate 541
Hilger (A.). Solanine and the Products of its Decomposition . . . 541
Hétet (F.). Sarracenia Purpurea 541
Schützenberger (P.). Researches on Albumin 542
Schroeder (H.). Specific Gravity Determinations of Solid Organic Compounds 610
Bernheimer (O.). Organic Ferricyanogen Compounds 611
Vincent (C.). Presence of Nitrils in the Distillate obtained by the Calcination of Residue from Beet-root Molasses 612
Pierre (J.) and E. Puchot. Products of Distillation of Alcohols . . 612
Riobinine and A. Saytzeff. Diallylisopropyl carbinol 612
Crié (L.). An Amyloïd Substance peculiar to the "Asques" of Pyrenomycetes 613
Thomsen (T.). Composition ot Wood. 613
Jousselin (L.). Nitrosoguanidine 613
Byk (S.). Removal of Sulphur from Guanidine Thiocyanate . . . 614
Lieben (A.) and S. Zeisel. Croton Aldehyde and its Homologues . . 615
Hartwig (E.). Oil of Wine. 615
Balbiano (L.). α-Isochlorobutyric Acid and its Derivatives . . . 615
Hill (H. B.). Di-substitution Derivatives of Acrylic Acid 616
ennett (W. Z.) and H. B. Hill. Dichloracrylic Acid 616
Schmidt (E.). Methylcrotonic and Angelic Acids. 617
Semlianitzine and A. Saytzeff. Oxyvaleric Acid from Allyldimethylcarbinol 618

PAGE

Schmöger (M.). Isomalic Acid 618
Mulder (E.). Synthesis of Dimethylbarbituric Acid 618
Böttinger (C.). Glyoxylic Acid. 619
Brunner (H.). Deoxalic Acid 619
Calm (A.). Constitution of Parabanic Acid 620
Andrianowsky (A.). Action of Aluminium Chloride on Acetic and Sulphuric Anhydride 620
Loir. Chemical Functions of Acetic Anhydride 621
De Forcrand. Formation of Glycocine from Ethyl Nitro-acetate . . 621
Councler (C.). Boron Compounds 621
Cahours (A.). Iodides of Stannopropyl 622
De Forcrand. Formation of Organic Ultramarines 622
Preis (K.) and B. Raymann. Action of Iodine on Aromatic Compounds with long Side-chains 623
Jacobsen (O.). Isocymene 624
Monnet (F.), F. Reverdin, and E. Nölting. Presence of Metanitrotoluene in Commercial Nitrotoluene 625
Monnet (F.), F. Reverdin, and E. Nölting. Influence of Metatoluidine in the Preparation of Rosaniline. 625
Wurster (C.). Nitrodimethylaniline 626
Panebianco (R.). Dimorphism of (1 : 4) Acetotoluide 626
Wurster (C.). Methyl-derivatives of Paraphenylenediamine . . . 626
Sendtner (R.). Action of Ethyl Oxalate on Dimethylparaphenylenediamine 627
Binder (F.). Dimethylparaphenylenediamine Carbamides 627
Baur (A.). Dimethylparaphenylenediamine Thiocarbamide. . . . 628
Koch (A.). Colouring Matters containing Sulphur derived from Dimethylparaphenylenediamine 628
Fahlberg (C.) and I. Remsen. Oxidation of Orthotoluene Sulphamide . 628
Griess (P.). Remarks on Weselsky's and Benedikt's Investigation on some Azo-Compounds 629
Schmidt (H.) and G. Schultz. Azo-, Azoxy-, and Hydrazo-Compounds . 630
Spica (P.). Propylphenols and other Derivatives of Propylbenzene . . 631
Barth (L.) and J. Schreder. Action of Fused Soda on Phenol. Synthesis of Phloroglucinol 633
Barth (L.) and J. Schreder. Oxidation of Resorcinol to Phloroglucinol . 633
Hessert (J.). Phthalyl Alcohol 634
Preis (R.) and B. Raymann. Cholesterin 634
Schultz (E.). Specific Rotatory Power of Isocholesterin 634
Fraude (G.). Orthocresolphthaleïn 634
Baeyer (A.). Diphenylphthalide and Phenylphthaleïn 636
Doebner (O.) and W. Wolff. Synthesis of Oxyketones 638
Fischli (H.). Paratoluic and Terephthalic Acids 638
Gabriel (S.) and J. Zimmermann. Dinitrohydrocinnamic Acid and its Derivatives 639
Oglialoro (A.). Phenylcinnamic Acid 640
Vulpius. Salicylates and their Application 641
Köhler (H.). Ethereal Oils of some Ericaceæ 641
Jacobsen (O.). Hydroxyparaxylic Acid 641
Saarbach (L.). Phenyloxypropionic Acid 642
Paternò (E.) and G. Mazzara. Cumolcarbonic Acid 642
Jacobsen (O.). Sulphaminemesitylenic Acid and a New Hydroxymesitylenic Acid 643
Gruber (M.). Action of Nitrous Anhydride on Protocatechuic Acid . . 643
Barth (L.). Dioxybenzoic Acids 644
Beilstein and Kurbatoff. Nitrophthalic Acid obtained by Oxidation of Nitronaphthalene 644
Anschütz (R.) and L. P. Kinnicutt. Phenylglyceric Acid 644
Freda (P.). Preparation of Digallic Acid 645
Schiff (H.). Digallic Acid 646

PAGE

CLAISEN (L.). Benzoic Cyanide and Phenylglyoxylic Acid 647
CLAISEN (L.). Amides of Phenylglyoxylic Acid 649
OTTO (R.). Sulphonic Acids derived from Sulphones 649
LENZ (W.). Fluobenzenesulphonic Acid, and the Melting Points of Substituted Benzenesulphonic Acids 649
SCHWARZ (H.) Formula of Hipparaffin 650
BERNTHSEN (A.) and H. KLINGER. Sulphine-compounds of Thiocarbamide 650
LANGE (A.). Diphenylthiohydantoïn 651
ARONHEIM (B.). Action of Nitrous Acid on Stannic Phenyl Chloride . . 651
SCHMIDT (H.) and G. SCHULTZ. Diphenols 651
SCHMIDT (H.) and G. SCHULTZ. Diphenyl Bases 652
SCHULTZ (G.). Constitution of Phenanthrene 653
LIEBERMANN (C.) and O. HÖRMANN. Anthrol 653
SCHUNCK (E.) and H. ROEMER. α- and β-Nitroalizarin and β-Amidoalizarin. 654
GRAEBE (C.). Alizarinsulphonic Acid 655
PICCARD (J.). Derivatives of Cantharadin and their Relation to the Ortho-series 655
FILETI (M.). Cinchonine 655
HESSE (O.). Conquinine Sulphate 656
SKRAUP (H.). Oxidation-products of Cinchona Bases 656
WEIDEL (H.). Berberine 656
TANRET (C.). Alkaloïds of the Pomegranate 657
PETIT (A.). A New Alkaloïd 658
SALKOWSKI (H.). Products of the Fermentation of Albuminoïds . . 659
HERTH (R.). Chemical Nature of Peptones 660
ZULKOWSKY (C.) Diastase and Beet Mucilage 660
PETRI (R.). Chondrin 661
LIPPMANN (E.) and J. HAWLICZCK. Eikosylene, a Derivative of Brown-coal Paraffin 699
NIEDERIST (G.). Action of Water on the Haloïd Compounds of Alcohol Radicles 700
LAUTERBACH (P.). Nitration of Derivatives of the Paraffins . . . 700
HAITINGER (L.). Nitrobutylene 700
EZWEILER. Researches on Perbromination 701
SCHÜLER (J.). Ferricyanides 702
LE BEL (J. A.). Limit of the Separation of Alcohol from Water . . . 703
LADENBURG (A.). Di-isobutylamine 703
WURTZ (A.). Bases derived from Aldol-ammonia 704
ANDREASCH (R.). Decomposition of Ammonium Formate by Heat . . 705
HELL (C.) and O. MÜHLHÄUSER. Addition-product of Acetic Acid with Bromine and Hydrochloric Acid 705
HELL (C.) and O. MÜHLHÄUSER. Addition-product of Acetic Acid with Bromine and Hydrobromic Acid 705
HELL (C.) and O. MÜHLHÄUSER. Action of Bromine on Acetic Acid . . 705
DUVILLIER (E.). Isomeride of Angelic Acid 706
KÖNIG (H.). Action of Hydrocyanic and Hydrochloric Acids on Ethyl Methylacetoacetate 706
CONRAD (M.). Substituted Malonic Acids 707
MORAWSKI (T.). Citramalic Acid 707
OST (H.). Pyromeconic Acid 708
GUARESCHI (J.). Ethylidene-disulphuric Acid 710
HOFMANN (A. W.). Angelylthiocarbimide 712
MALY (R.). Nitrosothiohydantoïn 712
RUDNEFF. Amides of Tertiary Hydrocarbon Radicles 713
FRIEDEL, CRAFTS, and ADOR. Durene-derivatives 713
HANHART. Action of Copper on Trichlorobenzene 714
WILLGERODT (C.). Action of Basic Compounds on Solutions of α-Dinitrochlorobenzene in Carbon Bisulphide 714
HANHART. Action of Chloroform and Perchloromethane on Dimethylaniline 714

PAGE

Hanimann and Hanhart. Desulphurisation of Dithiodimethyl-aniline . 714
Lippmann (E.) and W. Strecker. Amylidene-aniline 714
Hell (C.) and P. Schoop. Aniline Residues 715
Ladenburg (A.) and L. Rügheimer. Orthotolylene-diamine-derivatives . 715
Böttinger (C.). A New Base, $C_{19}H_{13}N_2$ 716
Higgin. Dibenzanilides 716
Willgerodt (C.). Preparation of Ethers of α-Dinitrophenol and α-Dinitrochlorobenzene 716
Trümpler (E.). Action of Soda-solution on Picramic Acid 717
Benedikt (R.). Tribromophenol Bromide and Tribromoresorcinol Bromide 717
Merz (V.) and G. Zetter. Preparation of Trinitroresorcinol and Trinitroorcinol 717
Sarauw. Action of Acetic anhydride and Sodium Acetate on Quinone . 718
Sommaruga (E. v.). Action of Ammonia on Quinones 718
Weselsky (P.) and R. Benedikt. Azophenols 718
Fileti (M.). Chemical Nature of the Essence of Laurocerasus and of Bitter Almonds 719
Tiemann (F.) and E. Helkenberg. Aldehydes from Orcinol and their Derivatives 719
Ladenburg (A.). Derivatives of Tropic Acid 720
Tiemann (F.) and C. L. Reimer. Umbelliferone Derivatives 720
Michaelis (A.). A Homologue of Phosphenyl Chloride 721
Zetter (H.), H. Ruoff, and Möe. Researches in Perchlorination . . 721
Labhardt (E.). Nitration of Bromonaphthalene 721
Beilstein and Kurbatoff. Oxidation of Nitronaphthalene 722
Smith (A. J.). Halogen Derivatives of β-Naphthol 722
Widmann (O.). Dichloronaphthalene-β-sulphonic Acid 722
Widmann (O.). Action of Chlorine on Naphthalene-β-sulphonic Chloride. A New Trichloronaphthalene 722
Pagliani (S.). Naphthylcarbamides 723
Perger (v.). α-Diamidoanthraquinone 724
Schunck (E.) and H. Römer. Nitroalizarin 725
Bruylants. Essence of Rosemary 725
Flawitzky (E.). Hydration of Terpenes 726
Montgolfier (J. de). Transformation of Camphic Acid into Camphor . 726
Sestini (F.). The Glucoside of Liquorice 727
Oglialoro (A.). Preliminary Notice on *Teucrium fruticans* . . . 728
Paternò (E.) and A. Oglialoro. Picrotoxin 729
Paternò (E.) and A. Oglialoro. Supposed Identity of Columbin and Limonin 730
Hilger (A.) and H. Bischoff. Colouring-matter of the Caryophyllaceæ . 730
Hoogewerff (S.) and van Dorp. Oxidation of Quinoline 731
Koenigs (W.). Oxidation of Cinchonine Quinoline by Potassium Permanganate 731
Andreoni (G.). Nicotine 731
Cahours (A.) and A. Etard. A New Nicotine Derivative 732
Ladenburg (A.). Tropidine 733
Ladenburg (A.). Artificial Atropine 733
Hofmann (A. W.). Piperidine and Piperine 733
Selmi (F.). Poisonous Alkaloïd from an Exhumed Corpse 734
Selmi (F.). Formation of Poisonous Alkaloïds in the Human Corpse . . 734
Lübawin (N.). Nucleïn from Cow's Milk 735
Liebermann (L.). Gas Evolved by the Action of Barium Hydrate on Albuminoïds 735
Guyard (A.). Copper and Ammonium Oxyferrocyanide 775
Claesson (P.). Methyl and Ethyl Sulphates 775
Sokoloff (N.). Preparation of Nitromannite and the Conditions of its Explosion 777
Salkowski (E.). Compounds of Grape-sugar with Cupric Hydrate . . 778

PAGE

Berthelot. Transformation of Sugar into Alcohol by a purely Chemical Method 778
Dieck (E.) and B. Tollens. The Carbohydrates of the Jerusalem Artichoke 778
Schmiedeberg (O.). A New Carbohydrate. 779
Girard (A.). Hydrocellulose 779
Grosheintz (H.). Tetrallylammonium Bromide and Triallylamine . . 779
Wurtz (A.). Bases derived from Aldol-ammonia 780
Lagermark (G.) and A. Eltekoff. Action of Sulphuric Acid on Acetylene 780
Köhler (K.). Substituted Nitrogen Chlorides 780
Rathke (B.). Diguanidine 781
Schalfeeff. Melissic Acid 782
Duvillier (E.). Dimethylacrylic Acid, an Isomeride of Angelic Acid . 782
Lagermark (G.). Synthesis of Tetrolic Acid 782
Giacosa (P.). Fermentation of Hydroxyvaleric Acid 782
Grimaux (E.) and J. Tscherniak. Preparation of Malonic Acid . . 782
Züblin (H.). Synthesis of Isosuccinic Acid 783
Seelig (E.). Derivatives of Mucic Acid 783
Wallach (O.) and P. Pirath. Thiamides of the Oxalic Acid Series . . 784
Grimaux (E.). Pseudouric Acid 784
Gustavson (G.). Interpretation of Reactions occurring in Presence of Aluminium Chloride 785
Gustavson (G.). Compounds of Cymene with Aluminium Bromide and Chloride 785
Balsohn (M.). Action of Ethylene on Benzene in Presence of Aluminium Chloride 785
Beamer (M.) and F. W. Clarke. Aniline Salts 785
Wallach (O.) and H. Bleibtreu. Thio-derivatives 786
Doebner (O.). Homologous Tertiary Diamines obtained in the Methylaniline Manufacture 786
Fischer (E. and O.). Remarks on Doebner's Communication on "Malachite-green" 787
Fischer (E. and O.). Dyes of the Rosaniline Group 787
Beamer (E.) and F. W. Clarke. Lithium Picrate 789
Baumann (E.) and L. Brieger. Formation of Cresols during Purification . 789
Baumann (E.) and L. Brieger. Paracresol 789
Clermont (P. de) and J. Frommel. Aurin 789
Wassermann (M.). Derivatives of Methyl-eugenol 790
Graebe (C.) and H. Bungener. Synthesis of Deoxybenzoïn . . . 790
Goldbeff (P.). Nitro- and Amido-derivatives of Deoxybenzoïn . . . 790
Böttinger (C.). Benzal Sulphide and Thiobenzaldehyde 791
Schall (C.). The Hydroxytoluic Acids from the Three Isomeric Cresols . 791
Meyer (R.). Derivatives of Hydroxypropylbenzoic Acid 795
Gabriel (S.) and A. Michael. Benzylmethylglycollic Acid . . . 795
Jaffe (M.). Acids produced by the Introduction of Chloro- and Bromo-benzene into the Animal System 796
Spiegelberg (L.). Nitro-, Amido-, and Bromobenzene-sulphonic Acids . 796
Heinzelmann and L. Spiegelberg. Pentabromobenzene-sulphonic Acid . 802
Baumann (E.) and C. Preusse. Bromophenylmercapturic Acid . . . 803
Fahlberg (C.). Liquid Toluenesulphonic Chloride and Beckurts' so-called Toluenemetasulphonic Acid 804
Rathke (B.). Aromatic Thiocarbamides 804
Rathke (B.). Action of Phenyl-thiocarbimide on Diphenyl-guanidine . 804
Hofmann (A. W.). Action of Phosphorus Pentachloride on Thiocarbimides 805
Baumann (E.) and F. Tiemann. Constitution of Indigo 806
Brieger (L.). Aromatic Products of the Putrefaction of Albumin . . 806
Beilstein and Kurbatoff. Oxidation of Bromonaphthalene . . . 807
Rosenstiehl. Absorption Spectrum of Alizarin and of some Colouring Matters derived from it 807
Graebe (C.) and H. Bungener. Synthesis of Chrysene . . . 807

PAGE

Dal Sie (G.). Active Principle of Insect Powder 807
Laiblin (R.). Nicotine and Nicotinic Acid 808
Skraup (Z. H.). Oxidation Products of Quinine 809
Skraup (Z. H.). Constitution of Cinchonine Bases 810
Latschinoff (P.). Oxidation of Cholic Acid 810
Egger (E.). Bilic Acid, an Oxidation-product of Cholic Acid . . . 810
Kossel (A.). Chemical Composition of Peptones 811
Hoppe-Seyler (F.). Lecithin and Nucleïn in Beer-yeast 811
Zeidler (O. and F.). Action of Oxidising Agents on the Olefines . . 907
Erlenmeyer (E.). The Two Isomeric Dibromopropanes 908
Berthelot. Direct Combination of Cyanogen with Hydrogen and the Metals 909
Prætorius-Seidler (G.). Reactions of Cyanamide 910
Schmitt (R.) and Goldberg. Action of Bleaching Powder on Ethyl Alcohol 910
Eder (J. M.). Behaviour of Gums and Carbohydrates towards Chromates under the influence of Light 911
Motten. Action of Heat on Sugar and Sugar Solutions 911
Girard (A.). Conversion of Hydrocellulose into Pyroxylin 911
Bunge (N.). Composition of Beet-root Gum 912
Duvillier (E.) and A. Buisine. Commercial Trimethylamine . . . 912
Vincent (C.). Distillation of Beet-root Residues 913
Custer (E.). Action of Ethyl Chlorocarbonate on Mono- and Di-amylamine 913
Jousselin (L.). Salts of Guanidine 914
Wurtz (A.). Chloral Hydrate 914
Landolph (F. H.). Action of Boron Fluoride on Acetone 914
Adrianowsky (A.). Action of Acetic and Sulphurous Anhydrides on Aluminium Chloride 915
Allihn (F.). Compounds of Ethyl Monochloracetoacetate 915
Toennies (P.). Conversion of Furfurangelic Acid into Azelaic Acid . . 915
Bouchardat (G.). Formation of Glycollic and Pyruvic Acids from Tartaric Acid 916
Miller (H. v.). Malonic Acid 917
Ficinus (O.). Preparation of Pure Tartaric Acid 917
Bell (C. J.). Action of Phosphorus Pentachloride on Saccharic Acid . 917
Conrad (M.). Ethyl Formyltricarbonate 918
Toennies (P.). Relation of Dibromopyromucic Acid to Mucobromic Acid . 918
Cahours (A.) and E. Demarçay. Stannopropyls and Stannisopropyls . 918
Cahours (A.) and E. Demarçay. Iodides of Stannobutyl and Stannamyl . 919
Wroblewsky (E.). Separation of Orthoxylene from its Isomeride, and a New Xylidene 919
Aschenbrandt (H.). Paradiethylbenzene from Paradibromobenzene . . 920
Michler (W.) and G. Moro. Action of Sulphochlorides on Amines . . 920
Rudolph (C.). Benzylamine 921
Rudolph (C.). Derivatives of Orthonitraniline 921
Fileti (M.) and A. Piccini. Decomposition of Phenylethylamine Hydrochloride 922
Michler (W.) and G. Blattner. Nitration of Benzene Sulphanilide . . 922
Bernthsen (A.). Amidines and Thiamides of Monobasic Organic Acids . 922
Hübner (H.) and E. Simon. Diethyl- and Diamyl-anhydrobenzyldiamidobenzene Compounds 923
Willgerodt (C.). Ethers of Trinitrophenol 923
Fischer (G.). New Colouring Matter from Orthamidophenol . . . 924
Schmitt (R.). Constitution of Dichlorophenol 924
Tiemann (F.). Relation between the Xylenols and some other Hydroxyderivatives of Benzene 924
Dale (R. S.) and C. Schorlemmer. Aurin 925
Otto (R.). Constitution of Sulphotoluide 926
Barth (L.) and J. Schreder. Fusion of Aromatic Acids with Soda . . 926

PAGE

TIEMANN (F.) and L. LANDSHOFF. Aldehydohydroxybenzoic Acids from Metahydroxybenzoic Acid 927
HÜBNER (H.). Iodosalicylic Acids 928
HÜBNER (H.), S. M. BABCOCK, and H. SCHAUMANN. Nitrosalicylic Acids and Dinitrophenols 928
GOLDBERG (A.). Parahydroxysalicylic Acid 928
GIACOSA (P.). Phenolglycollic Acid 929
BARTH (L.) and G. GOLDSCHMIDT. Ellagic Acid 930
RICHARDS (E. S.) and A. W. PALMER. Antimony Tannate 933
MULLER (F. H. S.) and F. WIESINGER. Preparation of Sulpho-compounds from Diazo-compounds 933
BARTH (L.) and M. v. SCHMIDT. Derivatives of α-Phenoldisulphonic Acid . 933
TED SCHI (V.). Resorcinoldisulphonic Acid 934
MICHLER (W.) and E. EXHERICH. Poly-substituted Carbamides. . . 934
MICHLER (W.) and R. ZIMMERMANN. Poly-substituted Carbamides . . 935
LACHMANN (G.). Tolylthiocarbimide 935
BAUMANN (E.) and F. TIEMANN. Constitution of Indigo 935
GIRAUD (E.). Derivatives of Indigotin 936
SUIDA (W.). Isatin Derivatives 937
BAEYER (A.). The Indigo-blue Group 937
MÖHLAU (R.). Orthodiamidodiphenethol 939
GREENE (H.). Preparation of Hexmethylbenzene from Acetone . . . 940
ADOR (E. A.) and J. M. CRAFTS. Action of Phthalic Anhydride on Naphthalene in presence of Aluminium Chloride 940
SCHMIDT (G. A.). Nitrophenanthrene and its Derivatives 941
LIEBERMANN (C.) and H. DEHNST. Constitution of Anthrarufin and Oxyanthrarufin 942
MORTON (H.). Chronology of the Isomeric Purpurins 943
TILDEN (W. A.). Compounds of the Terpenes with Hydrochloric Acid . 943
MONTGOLFIER (J. DE). Terebenthene Dihydrochloride 944
MONTGOLFIER (J. DE). Isomeride of Borneol 944
LIEBERMANN (C.) and S. HAMBURGER. Formulæ of Quercitrin and Quercetin 944
BAEYER (A.). Synthesis of Chinoline 946
HOOGEWERFF (S.) and W. A. VAN DORP. Oxidation of Quinine . . . 946
WEIDEL (H.) and M. v. SCHMIDT. Formation of Cinchomeronic Acid from Quinine, and its Identity with Pyridene-carbonic Acid 947
SKRAUP (Z. H.). Composition of Cinchonine 948
SKRAUP (Z. H.). Oxidation-products of Cinchonine 948
SKRAUP (Z. H.) and G. VORTMANN. Cinchonidine 948
HÜFNER (G.). Chemistry of the Bile 949
DRECHSEL (E.). Preparation of Crystalline Albumin Compounds . . 950
HOFMEISTER (F.). Regeneration of Albumin from Peptone 950
GAMGEE (A.) and E. BLANKENHORN. Protagon 950
TROOST (L.). Vapour-densities of certain High-boiling Organic Compounds 1025
PRUNIER (L.). Unsaturated Hydrocarbons from the Decomposition of American Petroleum 1025
ANSDELL (G.). Physical Properties of Liquid Acetylene 1028
LESCŒUR (H.) and A. RIGAUT. Solid Cyanogen Hydride 1028
LE BEL (J. A.) and GREENE. Action of Zinc Chloride on Normal Butyl Alcohol 1029
LE BEL (J. A.). Methylpropylcarbinol prepared by Synthesis . . . 1029
HANRIOT. Derivatives of Glycerol 1029
BOUTMY (H.). Researches on Nitroglycerol 1032
CLAESSON (P.). Ethereal Sulphates of Polyhydric Alcohols and Carbohydrates 1033
GÖTSCHMANN (T.). Methyl- and Dimethyl-diacetonamine 1035
CAHOURS (A.) and E. DEMARÇAY. Acids obtained by Distilling the Crude Acid from the Saponification of Fats in a Current of Steam . . . 1036
BURI (E.). Japanese Wax 1037

PAGE

Bourgoin (E.). Elimination of Bromine from Bromocitraconic Acid, and a New Organic Acid 1037
Odermatt (W.). Formation of Phenol from Putrefying Albuminoïd Matters 1038
Michael (A.). Synthesis of Phenol Glucoside and Orthoformyl Glucoside or Helicin 1038
Rush (W. B.). Copaibic Acid 1038
Troost (L.). Maximum Tension and Vapour-density of Alizarin . . . 1039
Bouchardat (G.). Identity of the Hydrates of Di-isoprene, Caoutchene, and Terpene 1039
Kachler (J.). Borneo Camphor 1039
Habermann (J.). Glycyrrhizin 1040
Mustapha (I.). Active Principle of *Ammi Visnaga* 1041
Flowers (H.). Lactucarium 1041
Costelo (D.). Gamboge 1042
Phipson (T. L.). Colouring Matter of *Palmella cruenta* 1042
Dragendorff and Stahre. Chemistry of the *Pæonia peregrina* . . 1043
Mandelin (A. F.). Quinine Citrate 1043
Hesse (O.). Paricine and Aricine 1044
Oudemans (A. C.). Quinamine 1044
Greenish (H. G.). *Bidara Laut* 1045
Arata (P. N.). Alkaloïd of Mio-Mio (*Baccharis cordifolia*) . . . 1045

Physiological Chemistry.

Duke Carl Theodor of Bavaria. Influence of the Temperature of the surrounding Air on the Excretion of Carbonic Acid and the Absorption of Oxygen in the Cat 74
Voit (C.). Influence of the Temperature of the surrounding Air on the Processes of Decomposition in the Organism of Warm-blooded Animals 75
Clermont (P. de) and J. Frommel. Magnesia as an Antidote for Arsenious Acid 77
Friedlander (C.) and E. Herter. Action of Carbonic Acid on the Animal Organism 174
Picard (P.). Researches on the Urea contained in the Organs . . . 175
Picard (P.). Albuminoïd Compounds of the Organs, and of the Spleen in particular 175
Salomon (G.). Occurrence and Origin of Hypoxanthine and Lactic Acid in the Animal Body 176
Jaffé (M.). Synthetic Processes in the Animal Body 176
Jonge (D. de). Secretion from the Sebaceous Glands of Birds . . . 176
Béchamp (J.) and E. Baltus. Modification effected by the Animal Organism on Various Albuminoïd Substances when Injected into the Veins . . 334
Pfeiffer (E.). Oxalic Acid not Poisonous (?) 335
Poincaré (L.). Danger of employing Methyl Alcohol in Certain Industries. 335
Wilckens (M.). Digestion in the Different Divisions of the Digestive Canal of the Sheep 391
Bertram (J.). Excretion of Phosphoric Acid by Herbivora . . . 392
Pott (R.). Researches on the Chemical Changes in the Fowl's Egg during Incubation 474
Schulz (H.). Action of Cacodylic Acid on the Animal Organism . . 476
Schulz (H.). Action of Mono- and Di-phenylarsenic Acid on Animals . 476
Seegen (J.). Transformation of Glycogen by the Salivary and Pancreatic Ferments 548
Quincke (G.). Formation of Emulsion, and the Influence of the Bile on Digestion 549
Béchamp (J.). Nature of the Albumins in Hydrocele 550
Schrodt (M.). Composition of Mares' Milk 550

PAGE

Jolly (L.). Distribution of Phosphates in the Blood 662
Salkowski (E. and H.). Physiological Relations of Phenylacetic and Phenylpropionic Acids 662
Dastre. "Starch Granules" and "Amyloides" of the Egg 662
Herter (E.). Tension of Oxygen in Arterial Blood 811
Henneberg (W.), E. Kern, and H. Wattenberg. Fattening of Sheep . 811
Kirchner (W. J.) and Du Roi. Beet-Leaves as Fodder for Cows . . 813
Salkowski (E.). Pancreatic Digestion 814
Bokay (A.). Digestibility of Nucleïn and Lecithin 814
Takácz (A.). Oxidation in the Organism 814
Baumann (E.) and C. Preusse. Oxidations and Syntheses in the Animal Organism 814
Eugling (W.). Composition of the Colostrum of the Cow 815
Bunge (G.). Behaviour of Potassium Salts in the Blood 816
Baumann (E.). Behaviour of Phenol in the Animal Organism . . . 816
Giacosa (P.). Action of Amyl Nitrite on Blood 816
Sonntag (E.), M. Schönberg, and H. Lorenz. Feeding Experiments with Sheep 951
Voit (C.) and C. Theodor. Influence of the Surrounding Temperature on the Tissue Metamorphosis of Warm-blooded Animals 951
Loew (O.). Source of Hippuric Acid in the Urine of Herbivorous Animals 952
Schmiedeberg (O.) and Walter. Formation of Urea in the Animal Organism 952
Renouard (A.). Analysis of Silk Cocoons 952
Nencki (M.) and P. Giacosa. Existence of Bacteria or their Germs in the Healthy Organs of Animals 1046
Wein (E.). Feeding of Calves without the Cow's Milk 1046
Hille. Poisoning of Fowls with Pumpkin Seeds 1046

Chemistry of Vegetable Physiology and Agriculture.

Heckel (E.). Influence of Salicylic Acid, Thymol, and some Essential Oils on Germination 172
Fitz (A.). Fungoïd Fermentation 172
Haas (B.). Ripening of Grapes 174
Mikosch (C.). Origin of Chlorophyll Granules 174
Kellermann (C.). Composition of the Growing Potato 174
Gayon (V.). Inversion and Alcoholic Fermentation of Cane Sugar . . 336
Bert (P.). Region of the Solar Spectrum which is Indispensable to Vegetable Life. 336
Müntz (A.). Ripening of Rye 337
Barral (J.). Nitrates in Beet-roots 337
Andreasch (R.). Ash of the Garden Pink and of the Rose . . . 338
Bemmelen (J. M.). Absorptive Power of Soils and of Silica . . . 339
Soyka J. Influence of Soils on the Decomposition of Organic Substances . 339
Just (L.). Influence of Temperature on the Germination of Seeds . . 393
Miquel (P.). Presence of an Alcoholic Ferment in the Air 394
Miquel (P.). The Succinic Fermentation 394
Hehner (O.). The Influence of Chloroform on Nitrification . . . 395
Warden (C. J. H.). Composition of Poppy Petal Ash 395
Schützenberger (P.) and A. Destrem. Researches on Beer-yeast . . 476
Schützenberger (P.) and A. Destrem. Composition of Beer-yeast . . 477
Thomson (W.). The Ferment produced by the Morbid Growth of the Bioplasm of the Yolk of Egg 478
Reichardt (E.). Distribution of Fungi 479
Corenwinder (B.). On the Banana 479
Schützenberger (P.) and A. Destrem. On Alcoholic Fermentation . . 550
Böhm (J.). Formation of Starch in Chlorophyll Grains in absence of Light 551

PAGE

Grosjean (H.). Analysis of some Fodders, and Observations on the Damage caused to Italian Beans by the Bean Insect 552
Bemmelen (J. M. v.). Absorptive Power of Soils 552
Béchamp (A.). Formation of Carbonic Anhydride, Alcohol, and Acetic Acid by Yeast alone, in presence and absence of Oxygen 663
Schiel (J.). Fermentation 663
Richet (C.). Conditions of Lactic Fermentation 663
Fitz (A.) Schyzomycetic Fermentation 664
Gunning (J. W.). Conditions of Life of the Lower Organisms . . . 664
Bancel (C.) and C. Husson. Phosphorescence of Lobster's Flesh . . 665
Bellucci. Supposed Existence of Hydrogen Peroxide in the Organism of Plants 665
Dehérain. Assimilation of Soda by Plants 666
Orth (A.). Constancy and Variation in the Composition of the Soil . . 666
Haberlandt (F.). Evaporation of Water from the Ground . . . 667
Ullik (F.). Absorptive Powers of Soils 667
Thaer. Experimental Inquiry as to the Quantity of Nitrogen which must be supplied to cultivated Plants to ensure their normal development as Field Crops 668
Bechamp (A.). Influence of Oxygen on Alcoholic Fermentation . . . 735
Freyberg (E.). Plant Respiration 736
Schmoeger (M.). On the Possibility of Replacing the Carbonic Acid of the Air necessary for the Production of Chlorophyll in Sarcophytic and Parasitic Plants by Organic Substances 737
Grete. Formation of Nitrites in the Soil 737
Hilger (A.). Chemical Composition of the Soils of the Vine-growing Districts of the Rhine and Maine 737
Heiden. On the Supply of Nitrogen to Plants 739
Miquel (P.). A New Organised Ferment 817
Macagno (J.). Action of the Ferment of Sour Wine on Good Wine . . 817
Gunning. Action of Alcohol on Bacteria 817
Occurrence and Vitality of Bacteria; Vitality of Yeast 817
Grandeau (L.). Influence of Atmospheric Electricity on Plants . . . 818
Pellet (H. P.). Ratio of the Sugar in the Beet to the Phosphoric Acid in the Root and Leaves 818
Gatellier (E.). Absorption of Atmospheric Nitrogen by Plants . . . 818
Tschaplowitz (F.). Absorption of Water by Leaves 819
Hoppe-Seyler (F.). A Simple Experiment to show the Evolution of Oxygen by Plants in Sun Light 819
Kellner (O.). Nitrogenous Constituents of Young Grass and Hay . . 819
Hilger (A.). Mineral Constituents of Horseradish 819
Porro (B.). Composition of Grapes at different Stages of Ripeness . . 820
Diseases of Cultivated Plants 820
Storer (F. H) and D. S. Lewis. Analysis of Weeds used as Salad . . 821
Leclerc (A.). Nutritive Value of Seed-bearing Beetroot 822
Pierre (J.). Oiling of Corn 822
Petermann (A.). Carrot Seeds 822
Vibrans (G.). Choice of Beetroot for Seeds 822
Wildt. Seeds of *Lallemantia iberica* 822
Wollny (E.). Ridge Cultivation 822
Drechsler (G.). Potato Cultivation 823
Moser (J). Cultivation of Dhurra or Sorgho Grass 823
Brimmer (C.). Action of Rain on Clover Hay 823
Otto and O. Knoch. Cultivation of Grass Seeds 824
Knop (W.). The Greenstone Soil of Berneck 824
Wollny (E.). Temperature of Soils 824
Ladureau (A.). Influence of the Time of Manuring in Beet Cultivation . 825
Ullik (F.). Agricultural Experiments on Irrigated Land 825
Moser (J.). Potassium Salts as a Manure 826
Ladureau (M. A.). Nitrates in Sugar Beets 826

PAGE

Christiani (W.). Effect of Manure on Crops 826
Doring and Bochmann. Effect of Artificial Manures on the Growth of Barley and on Meadow Land 828
Nencki (M.). Relation of Oxygen to the Life of the Microzoa . . . 953
Cameron (C. A.). Preliminary Notes on the Absorption of Selenium by Plants 955
Analyses of Cattle Fodder 956
Storer (F.) and D. S. Lewis. Seed of *Sorghum vulgare* 956
Storer (F.) and D. S. Lewis. Analysis of Shave Grass 956
Mutschler (L.) and C. Krauch. Composition of Candle Nuts . . . 957
Siewert (E.) Analyses of Hops 957
Haberlandt (F.). Cohesive Power of Soils 957
Lang (C.). Heat-capacity of Soils 958
Massenbach (G. v.). Experiments with Artificial Manures . . . 958
Wein (E.) and E. Ebermann. Manure Experiments with Bone-meal Superphosphate and with Potash Salts 959
Lintner (C.), Krandauer, and Treiber. Effect of Artificially Manured Barley on the Composition of the Wort 959
Moser (J.). Cultivation and Preservation of Maize 960
Gerland (W.) and J. Roberts. Preservation of Beet Leaves, and the Preparation of Brown Hay from Maize 960
Storer (F. H.) and D. S. Lewis. Analyses of some Species of the Gourd Family 961
Peckham (S. F.). Composition of the Ashes of Wheat Bran . . . 961
Koch. Method of Photographing Bacteria 1046
Cochin (D.). Non-existence of a Soluble Alcoholic Ferment . . . 1046
Bersch (J.). Cultivation of Pure Beer Yeast 1046
Davy (E. W.). Nitrification 1047
Briem (H.). Influence of Light on the Yield of Sugar-beets . . . 1047
Portele (R.). Influence of Heat on the Ripening of Grapes . . . 1047
Pedersen (R.). Influence of Temperature on the Evolution of Carbonic Anhydride by Barley Seeds 1048
Wurtz (A.) and E. Bouchut. Digestive Ferment of *Carica papaya* . . 1048
Wittmak (L.). Action of the Sap of *Carica papaya* 1048
Gayon and Millardet. On the Saccharine Matter contained in Vines suffering from Phylloxera 1049
Analyses of the Orange 1049
Lechartier (G.). Preservation of Green Fodder in Pits 1049
Kellner (O.). Nutritive Value of Malt 1050
Cottu (H.). Use of Sour Food for Cows 1050
Kleemann. Spent Hops as Fodder 1050
Liebscher, Briem, and R. Burger. Exhaustion of the Soil by Beet-root Cultivation 1050
Heinrich (R.). Artificial Manures 1050
Massenbach (v.). Experiments with Artificial Manures . . . 1050
Schaffert (F.). Experiments on Manuring 1050
Bochmann. Chili Saltpetre as a Manure for Barley 1051

Analytical Chemistry.

Bottomley (J.). Colorimetric Experiments 77
Hutchinson (C. C.). Schützenberger's Process for the Volumetric Estimation of Oxygen in Water 77
Hesse (O.). Appendix to the Estimation of Carbonic Acid in the Air . 78
Poleck and Biefel. Quantitative Determination of Sulphur in Illuminating Gas 78
Grete (E. A.). Estimation of Nitric Acid as Ammonia 79
Lunge (G.). Estimation of Nitrous and Nitric Acids 79
Laufer (E.). Behaviour of Quartz with Microcosmic Salt 79

PAGE

Davis (T. H.). Testing and Valuing of Gas Liquor 79
Wilson (H. M.). Remarks on the Estimation of Calcium Sulphate in Beer 79
Chapuis and Linnossier. Presence of Lead in Bismuth Subnitrate . . 80
Grete (E. A.). Estimation of Nitrogen in Nitrogenous Organic Bodies . 80
Adam (A.). New and Rapid Process for the Analysis of Butter . . . 80
Hager (H.). Butter Analysis 81
Lepel (F. v.). Adulteration of Wine 82
Neubauer (C.). Detection of Wines Adulterated with Grape-sugar . . 82
Vogel (H. W.). Testing Alizarin Colouring-matters and Green Aniline Colours 83
Lunge (G.). Application of Witt's Tropæolins to Titration . . . 176
Meyer (V.). Determination of Vapour-density 177
Donath (E.). Applications of Glycerin in Analysis 178
Böttger (R.). Reagent for Detecting Nickel 179
Reimann. Valuation of Body Colours 179
Hager (H.). Estimation of Alcohol and Extractive Matter in Wine . . 179
Maercker (M.). Gravimetric Estimation of Dextrose by means of an Alkaline Copper Solution 180
Heinrich. Estimation of Dextrose and Inverted Sugar in presence of Saccharose 180
Wurster (C.). Quantitative Estimation of Starch in Paper . . . 180
Hehner's Method of Testing Butter 181
Allen (A. H.). Distinctive Tests for Phenol, Cresol, and Creosote . . 182
Böttger (R.). Detection of Gypsum, Heavy Spars, &c., in Flour . . 183
Hofmeister (F.). Complete Precipitation of Albumin from Animal Fluids 183
Vielhaber (H. C.). Application of Phenol-phthaleïn 273
Stock (W. F. K.). Analysis of Boiler Feed-waters 273
Eder (J. M.). Estimation of Nitric Acid in Well Water 274
Finkener (R.). Estimation of Phosphoric Acid as Ammonium Phosphomolybdate 275
Smith (E. J.). Electrolytic Estimation of Cadmium 276
Beilstein (F.). Separation of Zinc from Nickel 276
Weil (F.). Further Note on Weil's Volumetric Method of Estimating Copper 276
Johnson (O.). Test for Arsenic 277
Morawski (T.) and J. Stingl. Volumetric Estimation of Manganese 277
Morawski (T.) and J. Stingl. Modification of Bunsen's Method of Manganese Determinations 278
Hempel (W.). Simultaneous Determination of Carbon, Hydrogeu, and Nitrogen in Elementary Analysis 278
Thresh (J. C.). Detection and Approximate Determination of Minute Quantities of Alcohol 279
Reichardt (E.). Detection of Chloroform 280
Vielhaber (H. C.). Estimation of Hydrocyanic Acid in Bitter Almond Water 280
Hesse (O.). Test for Quinine 280
Hesse (O.). Test for Quinidine 281
Hesse (O.). Behaviour of Potassium Thiocyanate with some of the Quinine Alkaloïds 281
Stoeder (W.). Estimation of the Alkaloïds in the Bolivian Quinine Barks exhibited at the Horticultural Exhibition in Amsterdam . . . 281
Bornträger (H.). Method for rapidly Incinerating Meal 282
Schmitt (E.). Testing Bees'-wax for Rosin 283
Pfeiffer (E.). Separation of the Alkaline Earths from the Alkalis . . 341
Kessler (F.). Estimation of Manganese, especially in its Alloys with Iron. 341
Weber (W.). Detection of Indican in Urine 342
Blas (M.). Detection of Salicylic Acid in Beer 342
Bornträger (H.). A New Indicator for use in Acidimetry and Alkalimetry 396

PAGE

Becker (G. F.). Reduction of Weighings in Air in Chemical Analysis to a Vacuum 396
Pillitz (W.). Analysis of the Zsadányer Meteorite 397
Pfeiffer (E.). Estimation of Nitric Acid by Potassium Dichromate . . 399
Castan (F.). Estimation of Minute Quantities of Soda in Potassium Nitrate 399
Leeds (A. R.). Alteration of Standard Ammonium Chloride Solution when kept in the Dark 400
Stingl (J.). Valuation of Burnt Lime 400
Fresenius (R.). Estimation of the available Zinc in Zinc-dust . . . 400
Klein (L.). Estimation of Carbon in Cast-iron 401
Donath (E.). Detection of Chromates and of Free Chromic Acid . . 401
Bronner. Use of Hempel's Lamp for illustrating Silver Assay as a Lecture Experiment 402
Bischof (G.). Estimation of Traces of Lead 402
Hurter (F.). Estimation of Cyanogen in Soda-lyes 402
Link (A.) and R. Mockel. On the Delicacy of some Reactions for Hydrocyanic Acid 403
Laugier (E.). Analysis of Raw Sugars 404
Neubauer (C.) and E. Borgmann. Estimation of Glycerin in Wine . . 404
Hüfner (G.). Estimation of Urea by means of Sodium Hypobromite . . 405
Stevenson (W.). Estimation of Quinine in Ferri et Quinæ Citras (B.P.) . 405
Wolfram (G.). Quantitative Determination of Theobromine in Cacao and Chocolate 406
Laugier (E.). Determination of Free Acids in Oils 406
Reichert (E.). Simplification of Hehner's Method of Testing Butter . . 406
Dietzell (B. E.) and M. G. Kressner. Testing Butter 407
Popper (R.). Quantitative Determination of Precipitates without Filtering, Washing, and Drying 480
Hehner (O.). Determination of Phosphoric Acid as Phosphomolybdate . 482
Young (W. C.). Note on the Detection of Alum in Flour by the Logwood Test 483
Stoddart (W.). The Logwood Test for Alum 483
Dupré (A.). Detection and Estimation of Alum in Wheat Flour . . 483
Doelter (C.). Estimation of Ferrous Oxide in Silicates 484
Cameron (C. A.). Estimation of Lead as Lead Iodate 484
Bayley (T.). Analysis of Alloys containing Copper, Zinc, and Nickel . . 485
Cameron (C. A.). The Inconstant Composition of Well-water . . . 485
Wigner (G. W.). Nitrogen Compounds present in Cereals 486
Siebold (L.). Titration of Hydrocyanic Acid and Cyanides, and its relation to Alkalimetry 486
Bardy (C.) and L. Bordet. Estimation of Methyl Alcohol in Wood Spirit 487
Cazeneune (P.). Detection and Estimation of Salicylic Acid in Animal Secretions 488
Dwars (B. W.). Determination of Quinine in certain of its Salts . . 488
Prunier (L.). Solubility of Cinchonine and Estimation of Cinchona Barks . 489
Mörner (K. A. H.). Alkali-albuminate and Syntonin 489
Cameron (C. A.). Amount of Solids in Milk 490
Williams (G.). Substitute for Litmus 553
Pusch. Böhr's Colorimetric Process for the Examination of Drinking-water 553
Hankó (W.). Modification of Simpson's Method for Estimating Nitrogen . 554
Schiff (H.). Analysis of Organic Compounds containing Halogens or Nitrogen 555
Wanklyn (J. A.) and W. J. Cooper. The Moist Combustion Process . 555
Perry (N. W.). Platinum Alloy Assay 555
Penney (M. D.). Alum in Flour and Bread 556
Pavy (F. W.). Volumetric Estimation of Sugar 557
Cazeneuve (P.). Estimation of Glucose in the Blood 557
Tollens (B.). Specific Rotatory Power of Cane-sugar 557

PAGE

Siewert (M.). Estimation of Fatty Matters in Feeding Stuffs . . . 558
Husson (C.). Examination of Coffee, Tea, and Chicory 558
Lindo (D.). Analysis of Caoutchouc 559
Hilger (A.). Detection of Ethyldiacetic Acid in Urine 560
Rüdorff (F.). Determination of the Specific Gravity of Powdered Substances 669
Hempel (W.). Estimation of Hydrogen in Gaseous Mixtures . . . 670
Guyard (A.). Separation and Estimation of Chlorine, Bromine, and Iodine 670
Otto (R.). Preparation of Sulphuretted Hydrogen for Chemico-legal Investigations 671
Clermont (P. de.). Action of Ammoniacal Salts on Metallic Sulphides, and its Application to Mineral Analysis 672
Wattenberg (H.). Estimation of Soluble Phosphoric Acid in Superphosphates 672
Beilstein (F.) and L. Jawein. Estimation of Zinc 672
Fesca (M.). Mechanical Analysis of Soils 673
Terreil (A.). New Method for Determining the Melting Points of Organic Substances 673
Mallard and Le Chatelier. Detection of Marsh-gas in the Air of Mines. 673
Gutkneckt (H.). Diagnosis of Fatty Alcohols 673
Picard (P.). Bernard's Method for the Estimation of Glucose in Blood . 674
D'Arsonval. Estimation of Sugar in Blood 674
Cailletet. A Test for Tartaric Acid which distinguishes it from Citric Acid 674
Hager (H.). Testing Milk for Starch Powder 674
Méhu (C.). Marchand's Method for Determining the Butter in Milk . . 675
Buchner. Adulteration of Beeswax 675
König (G. A.). Chromometry: an Application of the Blowpipe to Quantitative Analysis 740
Schöne (E.). Estimation of Hydrogen Peroxide 740
Reiset (J.). The Proportion of Carbonic Anhydride in the Air . . . 744
Wein. Estimation of Soluble Phosphoric Acid in Superphosphates . . 745
Beilstein (F.) and L. Jawein. Estimation of Cadmium 746
Smith (E. F.). Electrolytic Estimation of Cadmium 746
Rössler (C.). Estimation of Manganese 746
Hempel (W.). Fractional Combustion of Hydrogen and Marsh-gas . . 747
Regnauld (J.). Chloroform as an Anæsthetic 747
Pagliani (S.). Reaction of Salicylic Acid with Ferric Salts 748
Cazeneuve (P.). Separation and Estimation of Hippuric Acid . . . 748
Oglialoro (A.). Characteristic Reactions of Picrotoxin and of some of its Derivatives 748
Marchand (E.). Milk from Cows of Different Races 749
Settegast (H.). Contributions to Quantitative Spectrum Analysis . . 828
Penfield (S. L.). Volumetric Estimation of Fluorine 829
Schröder (W.). Estimation of Nitrogen in Urine 829
Salkowski (E.). Behaviour of Ammonium Chloride in the Organism and Estimation of Chlorine in Urine 830
Rammelsberg (C.). Determination of Lithium 830
Guyard (A.). Law peculiar to Metallic Ferrocyanides. 830
Smith (W.). Characteristic Reactions of the Aromatic Hydrocarbons with Antimony or Bismuth Trichloride 831
Casamajor (P.). Influence of Temperature on the Deviation of Polarised Light by Solutions of Inverted Sugar 832
Hehner (O.). Examination of Pavy's Method of Determining Glucose . 834
Dogiel (J.). Reactions of Albumin, and Behaviour of the Albumin of the Refracting Media of the Eye 834
Hüfner (G.). Estimation of Hæmoglobin and Oxygen in the Blood . . 835
Henneberg (W.). Determination of Fibrin 835
Loew (O.). Detection of Lecithin 835
Ruffle (J.). Estimation of Nitrogen 961

PAGE

Johnson (S. W.) and E. H. Jenkins. Determination of Nitrogen in the Analyses of Agricultural Products 962
Carnot (A.). Use of Sulphuretted Hydrogen in the Dry Way in Analysis . 963
Bohlig (E.). Water Analysis 963
Leeds (A. R.). Detection and Estimation of Nitrous Acid in Potable Waters, Acids, &c. 964
Johnson (S. W.) and E. H. Jenkins. Determination of Phosphoric Acid . 966
Albert (H.) and L. Siegfried. Estimation of the Value of Superphosphates 967
Dietzell (E.) and M. G. Kressner. Estimation of Phosphoric Acid in Fish Guano 968
Classen (A.). A New Quantitative Analytical Method of Manifold Application 969
Hertz (J.). Estimation of Silver, Chlorine, Bromine, and Iodine by Ammonium Thiocyanide 973
Wasowicz (M. v.). Verryken's Method of Detecting Metallic Poisons . 973
Playfair (D.). Note on the Detection of some Rare Metals in Pyrites Flue-dust 973
Drown (T. M.). Determination of Silicon in Pig-iron and Steel . . . 974
Rollet (A.). Determination of Sulphur in the Ore, in the Fuel, and in the Products of the Iron Industry 974
Clarke (F. W.). Electrolytic Estimation of Mercury 976
Lechartier (G.). Estimation of Organic Matter in Natural Waters . . 976
Petri (J.). Detection of Blighted Wheat in Flour by the Spectroscope . 977
Medicus (L.) and E. Schwal. Estimation of Starch in Sausages . . 979
Procter (H. R.). Weselsky's Reaction for Phloroglucin 979
Procter (H. R.). Determination of Free Acid in Tan Liquors . . . 980
Weigert (L.). Estimation of Acetic Acid in Urine 980
Nessler (J.). Detection of Free Tartaric Acid, and on Sulphuric Acid in Urine 981
Dwars (B. W.). On the Iodosulphates of the Quinine Alkaloïds . . . 982
Koettstorfer (J.). A New Method of Testing Butter for Foreign Fats . 983
Stein (G.). Analysis of Turkey-red Oil 984
Méhu (C.). Estimation of Urea 985
Schott (O.) Estimation of Iodine in Varec 1051
Estimation of Phosphoric Acid in Artificial Manures 1052
Millot (A.). Insoluble Phosphoric Acid in Superphosphate . . . 1052
Precht (H.). Volumetric Estimation of Magnesium 1053
Mann (C.). New Volumetric Method for Estimating Zinc 1054
Classen (A.). Estimation of Cobalt, Nickel, and Zinc by Precipitation as Oxalates 1054
Classen (A.). Separation of Manganese from Zinc 1055
Classen (A.). New Method of Separating Ferric and Aluminium Oxides from Manganese 1055
Nilson (L. F.). Criticism on Bunsen's Older Method for Separating Arsenic from Antimony 1058
Tornöe (H.). Results of the Norwegian Expedition to the North Sea . . 1060
Reynolds (J. E.). Sugar as a Test of the Purity of Water . . . 1062
Leeds (A.). Estimation of Nitrates in very Dilute Solution . . . 1062
Allen (A. H.). Petroleum-spirit and Benzene 1063
Hempel (W.). Limit of Detection of Carbonic Oxide 1063
Plugge (P.). Decomposition of Mercuric Cyanide by Dilute Acids, alone and in Presence of Sodium Chloride 1064
Waage (P.). The Ebullioscope 1065
Steiner (J.). The Ammoniacal Copper Test and its Application . . . 1066
Esbach (G.). Estimation of Urea in Urine 1067
Tattersall (J.). New Test for Papaverine 1067
Watson (W. H.). Detection of Milk Adulteration 1068
Soxhlet (F.). Quantitative Estimation of Milk Fat 1068
Blyth (A. W.). Composition of Devonshire Cream 1068

PAGE

Koettstorfer (J.). New Method of Detecting Foreign Fats in Butter . 1069
Perkins (F. P.). Analysis of Butter Fat 1070

Technical Chemistry.

Eyndhoven (J. van). Gaslighting 85
Tichborne (C. R. C.). Some Peculiarities of the Vartry Water, and the action of that Water on Boiler-plates 85
Schiff (H.). Preservation of Potable Waters 85
Fischer (F.). Utilisation of Suint from Wool 86
Analyses of Clays 87
Ireland (J.). Blair's Process for Iron Manufacture 89
Stead (J. E.). Phosphorus in Cleveland Ironstone and in Iron . . . 90
Steinau (R. and C.). Manufacture of a Red Pigment from Iron Scrap . 97
Cech (C. O.). Preparation of Rosemary-oil 97
Gayon (U.). Inactive Glucose in Crude Cane-sugars 97
Santos (J. R.). Analyses of Lamp-black made from the Natural Hydrocarbon Gas of the Ohio Petroleum Region 97
Simonin (L.). The Part played by Coal-dust in Producing Explosions in Coal Mines 98
Livache (A.). Abnormal Solubility of certain Bodies in Soaps and Alkaline Resinates 99
Kallab's New Bleaching Process for Animal Textile Fibres 99
Wittmack (L.). Advantages of only Partially Removing the Fat from Oil-Seeds 99
Gottfriedsen. On Tanning and Mineral Tanning 100
Intensifying Photographic Negatives by means of Potassium Sulphide . . 184
Preparation of finely divided Metallic Oxides 184
Wagner (R. v.). Numeïte, a New Jewel 184
Joclet (V.). Use of Chrome Alum instead of Potassium Dichromate in Wool-dyeing 185
Bell (I. L.). Separation of Carbon, Sulphur, and Phosphorus in Open Hearth, Puddling Furnace, and Bessemer-converter 185
Böttger (R.). Steeling Copper-plates 186
Biermann (E. W. L.). Manganese Alloys 186
Preparation of Inverted Sugar 187
Vaucher (G.). Ly-chô, a New Thickening Material 187
Müller-Jacobs (A.). Mordant for Turkey-red Dyeing 187
Prud'homme. Reduction of Indigo by Glycerin 188
Vulpius (G.). Behaviour of Vulcanised Caoutchouc with Illuminating Gas 188
Deite (C.). Iodine Industry in France 283
Gerlach (G. T.). Extraction of Sulphur by means of Superheated Steam . 284
Dixon (W. A.). Metallurgy of Nickel and Cobalt 285
Kern (S.). Purification of Cast Iron from Phosphorus 286
Kern (S.). Distribution of Manganese in Ferro-Manganese Alloys . . 286
Boussingault. Chrome-Steel 286
Keith's Process for Desilvering and Refining Raw Lead by Electrolysis . 288
Dixon (W. A.). Extraction of Gold, Silver, and other Metals from Pyrites 288
Estcourt (C.). Desirability of Fixing by Analysis some Standards of Value for Beer, based on the Qualities usually sold in Large Towns . . . 290
Weigert (L.). Clarifying and Preserving Wine 290
Bindschedler and Busch. Manufacture of Resorcin, Eosin, and other Derivatives of Resorcin 291
Deite (C.). Testing Lubricating Oils 292
Lewin (L.). Spongy Iron and Animal Charcoal as Materials for Purifying Water 343
Wolffhügel (G.). Carbon Monoxide in Foundry Furnaces . . . 344
Lawrence (R.) and C. W. Reilly. Analysis of Burton Ales and Dublin Porter 344

PAGE

On Cement 407
Terreil (A.). Analysis of Metallic Fragments obtained from Peruvian Tombs at Ancon (Lima) 409
Direct Preparation of Wrought Iron and Steel from Iron Ores . . . 409
Kern (S.). Working of Mild Steel 410
Keith. Process for Desilvering and Refining Raw Lead by Electrolysis . 410
Fischer (F.). Wearing of Steam Boilers 410
Berthollet. Explosive Mixtures of Air with Combustible Powders . . 412
Korschelt (O.). Saki, the Alcoholic Drink of the Japanese . . . 413
Aniline Blue 415
Alizarin Blue 419
Grawitz (S.). Action of Chromium Salts in presence of Chlorates . . 420
Witz (G.). Inactivity of Chromium Compounds in producing Aniline-black as compared with the Action of Vanadium Compounds 421
L'Hote (L.). Process for enriching Phosphates containing Earthy Carbonates 490
Löwig (G. and F.). Preparation of Alumina 490
Löwig (G. and F.). Preparation of Alkaline Aluminates 491
Cocx (L. C. W.). Solubility of Lime in Water in reference to the prescription for Aqua phagedænica 491
Hering (C. A.). Recovery of Antimony 491
Damage done to Barley by Sprouting in the Field 492
Blankenhorn (A.). Aëration of Must 492
Drevermann (A.). Recovery of Sugar from Calcium Saccharates . . 492
Wigner (G. W.). Nitrogenous Constituents of Cocoa 493
Wigner (G. W.). Some experiments with Silicated Carbon and Spongy Iron Filters 493
Gabba (L.) and O. Textor. Influence of the Chemical Composition of the Water used in the preparation of Raw Silk 493
Methylaniline 494
Grawitz (S.). Formation of Aniline Black by Chromates in presence of Chlorates 495
Ott (A.). On the Preparation of Paper for Pigment or Carbon Photography 560
Gluge (O.). Calcium Chloride 562
Benrath (H. E.). Macagno's Investigations on Bottle Glass . . . 562
Simonin (L.). A New Process for the Treatment of Iron and Copper Pyrites in the Dry Way 563
Fleitmann (T.). Preparation of Malleable Nickel and Cobalt, and the Application of these Metals 563
Coating of Metals with their Oxides to guard them against Atmospheric Action 563
Kern (S.). Action of Sea-water on Iron and Steel Plates 564
Use of Anthracite Dust in Du Puy's Process 564
Fischer (F.). Iron Smelting in the Cupola Furnace 564
Du Puy (C. M.). Direct Process for Making Wrought Iron and Steel . . 565
Müller (F. C. G.). The Bessemer Process 566
Kern (S.). Steel Making 567
Kern (S.). Manganese Steel. 567
Kern (S.). Preparation of Chrome Crucible Steel 567
Marcano (V.) and A. Muntz. Utilisation of the Banana 568
Deite (C.). Ghea Butter 568
Weigelt (C.). The Time of First Racking-off New Wines 569
Weigelt (C.). Dochnahl's New Method of Preparing Wine . . . 569
Schultze (W.). The Malt Test 569
Whewell (G.). Tenacity of Starch 570
Bindschedler and Busch. New Fast Green, or Malachite Green . . 571
Colouring Matters 571
Reimann (M.). Chrome Black on Wool 572
Beins (H.). Preparation of Carbonic Anhydride under any desired Pressure 676

PAGE

Lunge (G.). Antichlor 676
Wallace (R. W.) and C. F. Claus. Application of Gas Liquor to the Production of Potassium Carbonate and other Salts 677
Lunge (G.). Soda Industry 677
Preparation and Use of a highly Siliceous Pig-iron 678
Malleable Iron at the Paris Exhibition of 1878 679
Luca (S. de.). A Thread-like Substance found in the Excavations of Pompeii 680
Gawalowski. A Process for Utilising the Residue from the Manufacture of Potassium Ferrocyanide 680
Kernlter (F.). On Making Red Wine 681
Nessler. Pressing of Red Wine 681
Pollacci (E.). Plastering of Wine 681
Bühric (H.). Cerium Aniline-black 682
Witz (G.). Value of Certain Chemical Agents in Dyeing with Aniline-black 684
A Black Lac for Metal and Wood 684
Ott (A.). Heliographic Printing 750
Lunge (G.). Soda Industry 751
Weber (R.). Composition and Durability of Glass 754
Extraction of Silver from the Fahl-ores of Baranca, Mexico 755
Jordan (P.). Preparation of Manganiferous Pig-iron 755
Raetz (T.). Enamel for Cast- and Wrought-iron 755
Hollway (J.). A New Application of Rapid Oxidation by which Sulphides are Utilised for Fuel 755
Bode (F.). Extraction of Copper by Wet Processes 757
Winkler (C.). Fire-damp in Collieries 760
Jaillard. Absorbing Power of Wood Charcoal 761
Beyrich (C.). Process for Bleaching Vegetable Fabrics 761
Hilger (A.). Composition of "Grains" from Malt 761
Lunge (G.). The Amount of Sulphuric Acid in Wines 762
Pollacci (E.). Plastering of Wine 762
Berthelot. Changes which Wine undergoes when kept 763
Galimberti (A.). A Critical Point in Making Parmesan Cheese . . 764
Ott (A.). Photolithography 836
Wartha (V.). Hectograph and Chromograph 836
Mrowec (S.). Carbon Bisulphide Manufacture in Swoszowice and its Use for the Extraction of Sulphur 837
The Ammonia Soda Process in conjunction with the Manufacture of Gas . 837
Ramdohr (L.). Superheated Steam 838
Mactear (J.). Loss of Nitre in the Vitriol Manufacture 838
Pilter (T.). Decomposition of Phosphatic Minerals 839
Smetham (A.). Composition of a Boiler Incrustation 839
Tweedie (G. R.). New Method of producing a Coating of Magnetic Iron Oxide on Iron Surfaces 840
Köppen (E. v.). Physical and Chemical Changes which Spiegeleisen Iron undergoes when Smelted in the Cupola Furnace 840
Church (J. A.). Combustion in the Blast Furnace 841
Debrunner (H. G.). Third Form of Carbon in Steel 842
Beer Analyses 842
Stutzer (A.). Preparation of Pressed Yeast as a Bye-Product from Potato Spirit 843
Pilter (T.). Artificial Animal Charcoal 844
Pokormy (F.). Purification of Beetroot Syrup 844
Steffens, Manoury, Mateyczek, and Drevermann. Recovery of Sugar from Molasses 844
Weitz (M.). Crystallisation of Sugar and Preparation of Sugar Candy . 844
Abel (F. A.). Recent Contributions to the History of Detonating Agents . 846
Eder (J. M.). Examination of Chinese Tea 851
Manetti (L.) and G. Musso. Composition of Skimmed Whey . . . 856

PAGE

Eugling (W.) and v. Klenze. Alpine Dairy Produce 857
Duclaux (E.). Ripening and Decomposition of Cheese 858
Riessmüller (L.) and H. Wiesniger. Conversion of Rags and Hair into Manure 859
Haberlandt (F.). Strength of Hemp 859
Moeller (J.). Fibrous Materials 859
Grossman (J.). Softening Magnesia-hard Water 985
Bischof (G.). Sanitary Notes on Potable Waters 985
De Chaumont (F.). Experiments with Animal Charcoal, Silicated Carbon, and Spongy Iron Filters 986
Göbel (W.). Purification of Gas by Ammonia 986
König (D.). Decomposition of Bones by Steam 987
Joulie (H.). Retrogradation of Superphosphates 987
Douglas (T.). Green Pigment from Barium Chromate 987
Ilgen (O.). Solvay's Soda used in the Preparation of Ultramarine . . 987
Contributions to our Knowledge of Clays 988
Liquid Cyanides and Chlorides in Blast Furnaces 989
Patera (A.). Obtaining Vanadium from the Uranium Ore of Joachimsthal 989
Hesse (H.). Refining Copper 990
Weber (R.). Behaviour of Tin and Lead Alloys with Vinegar . . . 990
Smith (R. A.). Detection of Fire-damp 991
Sarrau and Vielle. Decomposition of Gun-cotton in a Closed Vessel . 991
Noble and Abel. Combustion of Gunpowder 992
Kjedal (J.). Rotatory Power of Beer Worts 993
Blankenhorn (A.) and H. W. Dahlen. Fermentation of Must . . . 993
Lunge (G.). Resin-sizing of Paper 994
Utilisation of the Residues obtained in the Manufacture of Aniline-red . . 995
Häusserman (C.). Manufacture of Methylaniline 995
Thoms (G.). Teak Wood 996
Quebracho Wood 996
Procter (H. R.). Explosive Product of Solution of Phosphorus in Carbon Bisulphide 996
Fleck (E.). Manufacture of Artificial Mother of Pearl and of Imitations of Marble from Glue 996
Heyden (F. v.) and T. Eckart. Preservation of Meat 996
Murro (G.) and A. Menozzi. Formation of Fat from Caseïn in the Ripening of Cheese 996
Fischer (F.). Heating Steam Boilers 1070
Gunning. Ferric Chloride as a Purifier of Water 1072
Schiff (H.). Preservation of Drinkable Water 1072
Morgan (T. M.). Composition of a Well-water at Grouville . . . 1072
Langbein (G.). South American Saltpetre 1073
Chemical Technology of Glass 1074
Arnold (A. E.). Phosphorus in Ancient Iron 1074
Head. Dephosphorisation of Pig-iron 1075
Bell (H. T.). Manufacture of Crucible Steel 1076
Bender (R.). Analysis of Alloys employed as Stopping for Teeth . . 1076
Biel (J.). Investigation of American and Russian Petroleum . . . 1076
Mott (H. A.). American Baking Powders and Alum 1077
Cloüet and Ritter. Arsenic in Grape-sugar 1077
Mach (E.). Experiments on the Fining of Wine 1078
Mader (C.). Apple and Pear Wine 1078
Markl (A.). Artificial Yeast for Molasses Distilleries 1078
Krandauer. Analysis of Waters for Brewing 1078
Müller (P.) and Hauer. Remarks on Beer Fermentation 1079
Holzner (G.). Researches on Beer 1079
Peckham (S. F.). Explosion of the Flour Mills at Minneapolis, Minnesota 1079
Sokoloff (N.). Explosion of Nitromannite 1080
Bechi. The Proper Time for Pressing Olives 1080

PAGE

Smith (W.). Extinguishing Fires in Tar Distilleries 1080
Falsky (F.). Salicylic Acid as a Preventative of House-fungus . . . 1080
Zerener (H.). Method of Preventing House-fungus 1080

Patents.

Duncan (J.), J. A. R. Newlands, and B. E. R. Newlands. Improvements in the Treatment of Sugar 421
Duncan (J.), J. A. R. Newlands, and B. E. R. Newlands. Improvement in the Treatment of Saccharine Substances or Compounds . . . 421
Holliday (J.). Improvements in Dyeing and Printing Aniline-black . . 422
Mactear (J.). Improvements in the Manufacture of Soda and Potash . 422
Cotte (E.). Improvements in the Manufacture of Certain Explosive Compounds 422
Brunner (H.). Improvements in the Manufacture of Alkali . . . 422
Lavender (R.). Improvements in treating Waste Sulphuric Acid that has been used for Pickling Iron Plates and other Articles of Iron or Steel . 425
Claus (C. F.). Improvements in the Manufacture of Sulphide and other Compounds of Zinc, and in the production of Bye-products resulting therefrom 423
Price (A. P.). Improvement in the Preparation and Treatment of Saccharine Substances and Compounds 423
Croll (A. A.). Improvements in the Manufacture of Sulphate of Alumina . 423
Wilkes (I.) and T. Johnson. Improvements in Purifying or Refining Copper 423
Vedova (F. G.). Improvements in the Manufacture of Materials containing Tannic Acid 496
Rickmann (J. P.). Manufacture of Ammonia 496
Haddan (H. J.). Treating Ores containing Silver and Copper . . . 496

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Differences in the Absorption Spectra of one and the same Substance. By H. W. Vogel (*Deut. Chem. Ges. Ber.*, **11**, 1562—1563).—This is a continuation of the dispute between Moser and the author as to whether "every chemical compound has its own spectrum." W. C. W.

An Improvement in the Peroxide of Manganese Battery. By Leclanché (*Compt. rend.*, lxxxvii, 329).—The author employs plates formed by the compression in a hydraulic press of a mass containing peroxide of manganese. These are attached to plates of retort carbon, and when exhausted by use, they may be replaced by fresh ones. The resistance in the cells may be diminished or increased in a suitable degree by using a greater or lesser number of the coupled plates, and under these conditions that resistance, being a function of the exciting liquid, tends to decrease. The cells, when sal-ammoniac is used, remain charged for an indefinite time, as there is no chemical action when the current is not closed. The depolarising action of the compressed plates is so great, that a mere fragment attached to a polarised carbon suffices to depolarise it completely in less than one minute. R. R.

Proof of the Statement that "Electrolytes are Salts." A Reply to L. Bleekrode. By W. Hittorf (*Ann. Phys. Chem.* [2], **4**, 374—416).—In consequence of Bleekrode's paper in the February number of the above Journal, in which he contradicts Hittorf's statement that electrolytes may be regarded as salts, the author in the present memoir passes in review the experiments and the deductions therefrom, which led him to the above-mentioned generalisation. The first portion of the paper is occupied with a long and minute review of the electrolytic work of various experimenters since Faraday. The investigations which he mentions are those of Berzelius, Davy, Daniell, Magnus, W. A. Miller, Matteucci, Becquerel, Bunsen, and Pouillet.

The remaining portion of the paper is a minute refutation of Bleekrode's criticisms. This is chiefly based on the author's own experiments published at various times in *Poggendorff's Annalen*.

J. M. T.

Relation between the Specific Heat at Constant Volume, the Temperature, and the Conductivity of Gases for Heat. By A. Wullner (*Ann. Phys. Chem.* [2], **4**, 321—341).—The greater part of this paper is occupied with a description of the methods employed in the experiments and by tabular statements of the results obtained.

The experiments detailed in the paper show that the relation between the different specific heats alters with the temperature. For those gases whose specific heat remains unaltered by the temperature, the pressure remaining constant, the change may be looked upon as similar to the change in the deviation of such gases from Mariotte's law. This is borne out by the fact, that the change is slightly greater in the case of carbon monoxide than it is in that of air. In the case of those gases with a specific heat changing with the temperature the relation of the specific heats varies to a much greater extent, and approximately in such a manner that the difference of the specific heats is constant at 0° and 100°. The total increase in the specific heat with increase of temperature may, the author thinks, be due to the work in the molecule.

As is mentioned at the outset of the paper, these experiments were undertaken for the purpose of showing that the discrepancy between the theoretical and experimental results of the values of the heat conductivity of different gases was caused by values being compared which were really not comparable. The following table gives the friction coefficient of several gases as determined by Obermaier, and the specific heats with constant volumes at 0° and 100°:—

	$\eta 0$.	$\eta 100$	C 0.	C 100.
Air	0·0001678	0·0002136	0·16902	0·16930
Carbonic oxide ..	0·0001625	0·0002047	0·17289	0·17395
Carbon dioxide ..	0·0001383	0·0001859	0·14886	0·16730
Nitric oxide	0·0001353	0·0001815	0·15130	0·17384
Ethylene.....	0·0009220	0·0001244	0·27007	0·35366
Ammonia	—	—	0·38026	0·41635

Winkelmann has determined the conductivity of the first five of the above gases between 5° and 8° C., and also the change caused by variation of temperature. In the following table (p. 3) the values calculated, according to Meyer's formula, and those experimentally found by Winkelmann, are compared.

The approximation between the calculated and experimental results in the case of these gases is as close as could possibly be expected, when the many different observations are taken into account upon which the calculated results rest. The greatest difference between theory and experiment is found in the case of air, but even here it is much lessened if the value of the coefficient of friction η_0 is taken equal to ·00018, when the calculated conductivity becomes ·0000469. This agrees closely with the number found by Kundt and Warburg.

	Conductivity.				$\frac{K_{100}}{K_0}$	
	At 0°, K_0.		At 100° K_{100}.			
	Calc.	Observed.	Calc.	Observed.	Calc.	Observed.
Air.....	0·0000434	0·0000513	0·0000553	0·0000653	1·2747	1·2770
Carbon monoxide.	0·0000430	0·0000499	0·0000545	—	1·2674	—
Carbon dioxide...	0·0000315	0·0000305	0·0000476	0·0000466	1·0516	1·5300
Nitric oxide	0·0000313	0·0000350	0·0000483	0·0000506	1·5413	1·4468
Ethylene.....	0·0000381	0·0000395	0·0000673	0·0000636	1·7668	1·6110
Ammonia	—	0·0000458	—	0·0000709	—	1·5475

J. M. T.

The Relation between Work effected by the Diffusion of Gases and the Second Law of Thermodynamics. By R. Clausius (*Ann. Phys. Chem.* [2], **4**, 341—343).—In *Nature*, vol. **17**, 202, Mr. Tolver Preston publishes a notice in which he states it as his belief that the phenomena he has observed in connection with the mechanical work obtained by the diffusion of gases are in contradiction to the second law of thermodynamics. The author in this paper shows that although at first sight this might appear to be the case, they are in reality in perfect harmony with it. The main part of Preston's argument is as follows:—He assumes a cylinder, in which there is a moveable piston of some porous substance, *e.g.*, pipeclay or graphite, each of the two parts of the cylinder separated by the piston being filled with a different gas, such as hydrogen and oxygen. Supposing now that at the beginning of the operation the gases are under the same pressure: a change, however, soon takes place on account of diffusion; the hydrogen passes through the piston more rapidly than the oxygen; and the quantity of gas on the hydrogen side becomes diminished, while that on the oxygen side is increased; at the same time the pressure becomes diminished on the hydrogen side and increased on the oxygen side, so that the piston will be set in motion. A certain amount of work is produced, and simultaneously the movement of the piston will cool the gas by expansion on the side from which it moves, and will heat it by compression on the side towards which it moves; heat, therefore, passes from a colder to a warmer body. Preston considers that the fact of obtaining work from heat without an initial difference of temperature, and the passing of heat from the colder to the warmer division, as contradicting the mechanical theory of heat.

Clausius, on the other hand, points out that if the conversion of heat into work and the passing of heat from the colder to the warmer body had taken place in this way, then the substances undergoing change at the end of the operation would necessarily be in the same state as they originally existed; then indeed a contradiction of the second law of thermodynamics would exist. But in the process, the substances undergoing change are the two gases; these are separate at the be-

ginning and mixed at the end: therefore, a change has taken place which compensates the conversion of heat into work, and the transference of heat from the colder to the warmer body. From the above, Clausius considers it apparent that, although the case in point has certain peculiarities which at first sight make it appear different from those generally investigated, it is in reality similar in all essential points, and contains nothing contradictory to the second law of thermodynamics. J. M. T.

Vapour-tension and Solidifying Point of Saline Solutions. By F. M. Raoult (*Compt. rend.*, **87**, 167—169).—The object of the author in these experiments was to determine the law, if any, which the vapour-tension and solidifying points of saline solutions follow. He determines the point of congelation according to Rudorff's method, operating with a solution of 4·5 grams of substance and 100 grams of water.

The vapour-tension is determined by two methods; (1) by placing two vapour barometers in a vessel of boiling water, the one for the salt solution, the other containing pure water; (2) a method founded on the determination of the boiling points of the saline solutions, by boiling them in a platinum retort having a reversed condenser. At the moment of determining the temperature, the ebullition is regulated by means of a gentle current of electricity. Under these conditions, the vapour-tension is given by the barometer.

If f = vapour-tension of saline solution at a given temperature, and f' that of pure water at the same temperature, and P the weight of anhydrous salt in 100 of water, and K the constant coefficient for the same salt through an interval of a few degrees, then—

$$f' - f = \mathrm{K}\mathrm{P}f.$$

This formula gives the value of K. K being determined, it is only necessary to multiply it by P × 760 to obtain the difference of the tensions $f' - f$ at the temperature of 100°. The results obtained by the two methods agreed to about $\frac{1}{20}$, and the author has taken the mean. To facilitate comparison of the numbers relating to the lowering of the freezing point and the diminution of vapour-tension, he has divided the results obtained by the weight of salt dissolved in 100° of water. The table given below shows: (1) that the difference of vapour-tension and the lowering of the solidifying point varies considerably with the nature of the salt dissolved; (2) the property of diminishing the vapour-tension and lowering the solidifying point of the different solutions seems to be the same for all the anhydrous salts, although differing in degree; (3) the property which anhydrous salts possess of producing both effects seems to be, as a rule, in the inverse ratio to the atomic weights.

Salt in solution.	Difference between the freezing point of pure water and that of a solution containing 1 part in 100 of water.	Difference at 100° between the tension of water vapour and that of a solution containing 1 part in 100 of water.
	°	mm.
Mercury bichloride ..	0·048	0·058 × 7·6
,, cyanide	0·059	0·087 × 7·6
Lead nitrate	0·104	0·110 × 7·6
Barium ,, ...	0·145	0·137 × 7·6
Silver ,, ...	0·145	0·160 × 7·6
Potassium ferricyanide	0·246	0·165 × 7·6
,, chromate ..	0·200	0·213 × 7·6
,, sulphate ..	0·210	0·201 × 7·6
,, iodide	0·215	0·225 × 7·6
,, chlorate ..	0·215	0·240 × 7·6
,, nitrate	0·245	0·280 × 7·6
Ammonium sulphate	0·273	0·230 × 7·6
Potassium bromide..	0·295	0·310 × 7·6
Sodium nitrate	0·347	0·380 × 7·6
Ammonium nitrate..	0·378	0·361 × 7·6
Potassium chloride ..	0·446	0·450 × 7·6
Sodium ,, ..	0·600	0·604 × 7·6
Ammonium ,, ..	0·639	0·565 × 7·6

J. M. T.

Measurement of the Heat developed in the Formation of Hydrogen Phosphides and Arsenides. By J. Ogier (*Compt. rend.*, **87**, 210—213).—The reaction of bromine with phosphine easily affords thermic measurements, care being taken to use an excess of bromine. The reaction may be expressed by the following equation:—$PH_3 + 8Br + 5HO = PO_5 + 8HBr$. For the determinations the author used a water calorimeter, in which he placed the tube containing the Br under a layer of water. The phosphine, carefully freed from liquid phosphide, was passed in by displacement. In this way it was found that the heat disengaged by the action of bromine on one equivalent of $PH_3 = 254·6$ thermal units. From these numbers the heat disengaged by the formation of PH_3 may be deduced by observing that the same final result is obtained by both the following cycles of reactions:—

First series.

$P + H_3$ heat disengaged		x
$5(H + O)$	,, ...	$A = + 147·5$
$PH_3 + 8Br$	,, ...	$B = + 254·5$

Second series.

$P + O_5$ disengaged	$C = + 202·7$ (Thomsen).
$8(H + Br)$ disengaged....	$D = + 236·0$ (Berthelot).

from which $x = (C + D) - (A + B) = +36·6$ heat-units, being the heat developed in the formation of PH_3 from its elements.

The author has by analogous processes measured the heat produced in the formation of P_2H, the solid phosphide of hydrogen obtained by

the action of hydrochloric acid on the spontaneously inflammable gas. In contact with bromine and water that body is decomposed as follows: $P_2H + 11Br + 10HO = 2PO_5 + 11HBr$.

The experiment gave an average of 367·2 heat-units, from which the number +66·7 heat-units is deduced for the formation of P_2H.

The same methods are applicable to the heat of formation of hydrogen arsenide, and the number found for the formation of AsH_3 from its elements is −11·7 heat-units. The following table

	Heat-units.
$N + H_3 = NH_3$	= + 26·7 (Favre Thomsen).
$P + H_3 = PH_3$	= + 36·6
$As + H_3 = AsH_3$	= − 11·7

shows, according to the author, that the thermic effect is directly proportionate to the relative stability of these gaseous hydrides. He then compares the three chlorides with the hydrides, and finally the oxides with the hydrides, showing in all cases that the relation between the thermic effect and the stability holds good. J. M. T.

Thermo-chemical Researches: Heat of Solution of Nitrates, Sulphates, Dithionates, and some other Salts. By J. Thomsen (*J. pr. Chem.* [2], **17**, 165—183).—This paper is a continuation of one of which an abstract appeared in this Journal, 1877, ii, 693. The results of the experiments are given in a table, from which it appears that—

The *anhydrous* salts exhibit in some cases a positive, in others a negative heat of solution, and follow the same laws as the haloïd compounds. The propositions stated in the previous paper may therefore have the following general form:—

a. Those anhydrous salts, chlorine-, bromine-, and iodine-compounds, which dissolve in water with *development* of heat, form crystallised compounds with water (or are fully decomposed).

b. Those salts, chlorine-, bromine-, and iodine-compounds, which form no crystallised compounds with water (or are not fully decomposed) dissolve in water with *absorption* of heat.

The converse of the latter of these propositions is not true, for NaBr, SrN_2O_6, and $Na_2S_2O_6$ dissolve in water with absorption of heat, and yet form crystalline compounds with it. Positive heat of solution, however, is always a proof of affinity for water, which may give rise to compounds with it. Potassium salts are generally anhydrous. Sodium salts show a greater affinity for water than potassium salts, and there are consequently more anhydrous sodium salts which are soluble with development of heat. The anhydrous salts of the magnesium group of metals have all a positive heat of solution, and combine easily with water, whilst many salts of lead, thallium, and silver form no hydrates, and therefore dissolve with absorption of heat.

Of *hydrated* salts the majority absorb heat on solution, but there are a good many exceptions. The reason of this seems to be that these last are not fully saturated as regards water, and that compounds containing more water are possible.

The heat of *formation of hydrated salts* is very various, and depends

partly on the number of water molecules, partly on the nature of the salt. The following instances may be adduced:—

	Formation of hydrate.
($Na_2HPO_4.12H_2O$)	28470 units of heat.
($Na_4P_2O_7.10H_2O$)	23520 ,,
($Na_2CO_3.10H_2O$)	21800 ,,
($Na_2SO_4.10H_2O$)	19220 ,,
($MgSO_4.7H_2O$)	24070 ,,
($CuSO_4.5H_2O$)	18550 ,,
($CaN_2O_6.4H_2O$)	11200 ,,
($SrN_2O_6.4H_2O$)	7680 ,,
($Li_2SO_4).H_2O$	2640 ,,

Regularity in magnitude of heat of solution of the salts is not very apparent, but still it does exist; for instance, the difference of heat of solution of equivalents of anhydrous nitrates and sulphates of potassium, sodium, thallium, and ammonium is approximately the same.

	R = K.	R = Na.	R = Tl.	R = NH_4.	
R_2SO_4 ..	− 6380	+ 460	− 8280	− 2370	heat-units.
$R_2N_2O_6$..	−17040	−10060	−19940	−12640	,,
Difference	10660	10520	11660	10270	,,

The haloïd compounds show great regularity in the difference of the heats of solution of analogous compounds. The difference between the heats of solution of the chlorine-, bromine-, and iodine-compounds of sodium and those of potassium is as 2 : 3 : 4.

$$Na_2Cl_2—K_2Cl_2 = 6520 = 2 \times 3260$$
$$Na_2Br_2—K_2Br_2 = 9780 = 3 \times 3260$$
$$Na_2I_2—K_2I_2 = 12660 = 4 \times 3165$$

The differences in the case of the haloïd compounds of lead and silver are as 4 : 5 : 6.

$$PbCl_2—Ag_2Cl_2 = 24900 = 4 \times 6225$$
$$PbBr_2—Ag_2Br_2 = 30160 = 5 \times 6032$$
$$PbI_2—Ag_2I_2 = 36400 = 6 \times 6067$$

These numbers are nearly double of the differences between sodium and potassium.

The chlorides of lithium and sodium show a difference three times as great as that between sodium and potassium chloride.

$$Li_2Cl_2—Na_2Cl_2 = 19240 = 6 \times 3207$$
$$Na_2Cl_2—K_2Cl_2 = 6520 = 2 \times 3260$$

Magnesium, calcium, strontium, and barium give numbers which stand as 6 : 2 : 3.

$$MgCl_2—CaCl_2 = 18510 = 6 \times 3085$$
$$CaCl_2—SrCl_2 = 6270 = 2 \times 3135$$
$$SrCl_2—BaCl_2 = 9070 = 3 \times 3023$$

The hydrated compounds are—

$$CaCl_2.6H_2O—SrCl_2.6H_2O = 3160 = 1 \times 3160$$
$$CaBr_2.6H_2O—SrBr_2.6H_2O = 6110 = 2 \times 3055$$

Copper, barium, and tin show the following differences :—

$$CuCl_2—BaCl_2 = 9010 = 3 \times 3003$$
$$CuBr_2—BaBr_2 = 3270 = 1 \times 3270$$
$$CuCl_2.2H_2O—BaCl_2.2H_2O = 9140 = 3 \times 3047$$
$$CuCl_2.2H_2O—SnCl_2.2H_2O = 9580 = 3 \times 3193$$

Zinc and cadmium :—

$$ZnCl_2—CdCl_2 = 12620 = 4 \times 3155$$
$$ZnBr_2—CdBr_2 = 1 \times 4590$$
$$ZnI_2—CdI_2 = 12270 = 4 \times 3068$$

The differences between aluminium, iron, and gold are—

$$Al_2Cl_6—Fe_2Cl_6 = 90330 = 5 \times 18066 = 30 \times 3011$$
$$Fe_2Cl_6—Au_2Cl_6 = 54460 = 3 \times 18153 = 18 \times 3025.$$

Phosphorus, arsenic, and antimony give—

$$PCl_3—AsCl_3 = 47560 = 5 \times 9512 = 15 \times 3171$$
$$AsCl_3—SbCl_3 = 9410 = 1 \times 9410 = 3 \times 3137$$

G. T. A.

Inorganic Chemistry.

Preparation of Chlorine and Hydrochloric Acid by means of Calcium and Magnesium Chlorides. By E. Solvay (*Chem. Centr.*, 1878, 336).—The above-mentioned chlorides are mixed with silica and alumina or silicate of alumina, and dried. To obtain chlorine they are intensely heated in a current of air; for HCl they are heated in a current of superheated steam. Silicates and aluminates of lime and magnesia are formed as bye-products in this process, and may be used for making chloride of lime and precipitated silica and alumina, also for making chlorine from hydrochloric acid, and for soda manufacture by the ammonia process. J. M. T.

Hydrochloric Acid containing Phosphoric Acid. By E. Holdermann (*Arch. Pharm.* [3], **13**, 100—103).—A sample of hydrochloric acid gave when tested all the reactions for purity, so that when evaporated over a bare flame in a platinum vessel it left a barely perceptible residue, but when iron was dissolved in the acid, a white precipitate was formed, which on examination was found to be due to a large quantity of phosphoric acid present. It is, therefore, advisable, when testing for phosphoric acid by volatilisation, to evaporate the liquid in a watch-glass over the water-bath.

E. W. P.

Ozone. By Jeremin (*Deut. Chem. Ges. Ber.*, **11**, 988).—The author finds that ozone dissolves to a considerable extent in aqueous oxalic acid, forming a solution which keeps indefinitely. A solution which has been kept some time is a better disinfectant than when

fresh. In the gaseous state ozone keeps better in the light than in the dark. For washing with ozone the author constructs stoppers, stopcocks, tubes, &c., of a composition of powered pumice, paraffin, wax, and resin, which is not acted on by ozone. For experiments with substances which attack paraffin he recommends a composition of gelatine and glycerin. J. R.

Oxidation of Nitrous Acid by Ozone and by Moist Oxygen. By BERTHELOT (*Ann. Chim. Phys.* [5], **13**, 367—368).—In an acid solution nitrous acid is at once oxidised to nitric acid by ozone, which may be exactly determined by this means. A standard solution of a nitrite is acidified and shaken with a gas containing ozone, which oxidises the nitrous acid and is itself absorbed. The excess of nitrite in the solution is then titrated with potassium permanganate. In presence of alkalis, the ozone is destroyed without acting on the nitrous acid. Moist air also slowly oxidises nitrous acid. Dry oxygen or ozone converts nitrous acid into nitrogen tetroxide, which in presence of water yields nitric acid. It is thus clear that the presence of nitrous acid and ozone simultaneously in the air is not possible.

L. T. O'S.

Presence of Ammoniacal Salts in Sea-water. By M. L. DIEULAFAIT (*Ann. Chim. Phys.* [5], **13**, 374—409).—The presence of ammoniacal salts in sea-water was first pointed out by Marchand (*Mem. Acad. Med.*, **19**, 1855), and subsequently investigated by Boussingault (*Agronomie. Chim. Agrie et Physiol.*, 208), and Forchammer (*Phil. Trans.*, **155**, 203). The author has made fresh determinations of the ammonia present in sea-water; also of its deposits, employing Boussingault's method with slight modifications.

Water from the Mediterranean.—This water was taken south of Marseilles, 12 kilometers from the shore, and about the meridian of Aix. 10 litres were distilled and 4 litres collected and redistilled. 800 c.c. of the second distillate are again distilled, and the ammonia determined in the first 300 c.c. which come over. In this manner the result obtained was ·221 mg. NH_3 per litre.

From water taken between Marseilles and China at depths varying from 1·5 to 2 metres, the following results were obtained:—

	mg. NH_3 per litre.
Ismaila	0·204
Red Sea, long. E. 33° 54′, lat. N. 24° 4′	0·176
Cape Gardafuy, long. E. 49° 42′, lat. N. 12° 44′	0·176
Socatora, north of the island	0·176
Bay of Bengal, long. E. 87° 55′, lat. N. 5° 34′	0·136
Coast of Cochin China, long. E. 107° 22′, lat. N. 14° 37′	0·340

From these results it is seen that ammonia occurs in seas of all latitudes.

The quantity of ammonia in the sea-water does not increase proportionally to the evaporation of the water, inasmuch as a portion of the ammonia escapes into the air.

The Ammonia in the Deposits from Sea-water.—During the evaporation of the water in saline marshes, deposits are formed, the first consisting of pure crystallised gypsum covering the surface of the pan,

whilst the second is a black mud, obtained partly by the decomposition of the "feutre," the term applied to the "stratum" of algæ which covers the bottom of the salt-pans. There is also a greenish-yellow liquid obtained, which contains some of the refuse of the mud and a large quantity of gypsum.

Each of these contained ammonia in the following proportions:—

Gypsum	1·6 mg.	NH_3 per kilo.
Black mud	8·3 „	„
Liquid	3·4 „	per litre.

The water of the pool of Lavaldue contains 250 times more ammonia than the water of the Seine at Paris, and 50 times more than that of the Bievre, on the banks of which many manufactories stand.

By the evaporation of the sea-water, deposits are obtained; in the first place calcium carbonate, mixed with oxide of iron and strontium carbonate, separates out, but the more important deposits are those of gypsum, which are two—(1) pure gypsum, and (2) gypsum mixed with calcium carbonate and some mud, imparting to it a grey colour. There is also a deposit of mud. These last three absorb ammonia, which the author has determined in twenty samples obtained from different places to the south of France. The results, of which the following are examples, show the variation in the quantity of ammonia:—

Triassic.	Pure gypsum. mg.	Grey gypsum. mg.	Black mud. mg.
Simiane (Bouches du Rhone) ..	1·2	6·2	15·0
Saint Julien	1·6	2·6	12·2
Castellane	2·4	3·6	14·0
La Palud	0·8	3·1	11·2
Taulanne.....	1·4	3·0	12·7
Solliès (Ville)	1·9	3·1	14·0
Le Beausset	3·2	4·3	11·1
Le Faron (Toulon)	1·8	4·8	12·9
Bandol.....	2·2	4·6	14·5

The author has also examined some gypsum beds of the tertiary formation for ammonia, and finds that they correspond with the grey gypsum above, having given the following results:—

Bois d'Asson	4·04 mg.	NH_3 per kilo.
Saint Jean de Garquier ..	2·14 „	„
Camoins	2·87 „	„

The presence of ammoniacal salts in the gypsum accounts for the disengagement of ammonia in the manufacture of plaster of Paris.

The boric acid emitted by the lagoons in Tuscany is often accompanied by ammonia, which may be explained if it is admitted that the boric acid exists in the saline beds of the lagoon, which absorb ammonia, and that the part played by the volcanic agent is purely mechanical, whereas on the contrary, by assuming the boric acid to have a volcanic origin, the presence of ammonia cannot be explained.

The water of Lake d'Enghien contains only 0·07 mg. NH_3 per litre, whilst the sulphur spring fed by the lake contains 5·06 mg. per litre.

This is due to the fact that the water on emerging from the lake has to pass over sediments, from which it dissolves the ammoniacal salts.

The author is of opinion that all saline waters obtain their mineral matter from the two salt-bearing formations, the trias and tertiary, which always contain a considerable quantity of ammoniacal salts, and the conclusion he draws is that all saline mineral waters ought to contain abnormal quantities of ammoniacal salts, whether they be sulphurous or not, thermal or not. L. T. O'S.

Chemical Action of Water and Saline Solutions on Zinc. By A. J. C. Snyders (*Deut. Chem. Ges. Ber.*, **11**, 936—949).—The author has examined the action of water and of saline liquids on zinc under various conditions. His results are summed up as follows:

1. Zinc decomposes saline solutions, whether concentrated or dilute, without access of oxygen, evolving hydrogen and forming zinc oxide.

2. Solubility of zinc oxide in the saline liquids promotes the action.

3. Zinc oxide dissolves in solutions containing 1 per cent. or less of salt. The solubility varies with different salts, being greatest with ammonium salts. Zinc hydrate and carbonate are insoluble in carbonates. The solubility of zinc oxide increases with the strength of the solutions and with the temperature.

4. When a saline liquid is saturated with zinc oxide, the decomposing action still goes on, the oxide then formed remaining undissolved.

5. In presence of oxygen free from carbon dioxide, the zinc oxide dissolves more readily, on account of the direct oxidation of the metal.

6. In presence of the carbon dioxide of the air, the solvent action is to some extent prevented, owing to the formation of basic carbonate.

7. The solvent action is strongest with chlorides and potassium sulphate, weaker with alkaline and barium nitrates and magnesium sulphate.

8. Solutions of alkaline carbonates and sodium phosphate do not act on zinc protected from the air. Even in presence of oxygen, solutions containing 1 per cent. of these salts dissolve but little zinc, because the carbonate or phosphate first formed protects the metal from further action. Nevertheless, traces of zinc oxide are dissolved by still weaker solutions.

9. The solvent action is greater at higher temperatures: at 0° it is very slight.

10. Solutions of ammonium salts take up more zinc oxide than solutions of salts of fixed alkalis. The surface of the metal remains clean, and nothing is deposited from the solution, even in presence of oxygen.

11. Hard waters do not act on zinc, even when rich in chlorides and sulphates. Soft waters dissolve the more zinc the greater the preponderance of chlorides, sulphates, and nitrates over carbonates and phosphates contained in them. J. R.

A New Earth of the Cerium Group, and on the Analysis of Natural Niobates. By J. L. Smith (*Compt. rend.*, **87**, 146—148).—The object of this paper is to call attention to the use the author made of concentrated hydrofluoric acid for decomposing niobates; its action on samarskite and euxenite being as energetic as that of hydrochloric acid on calcium carbonate. By the action of the acid, all the metallic acid forming oxides, together with the oxides of iron and manganese, are dissolved, whilst the insoluble portion contains all the earths and the uranium oxide. The presence of tantalates renders the decomposition more difficult. In a former memoir, the author divided the earths contained in Carolina samarskite into the yttrium and cerium groups, pointing out however that the latter group might not contain cerium oxide, and that thorium could not be detected in it with certainty. Since this, he has found that the yttrium group contains about two-thirds of yttrium and one-third of erbium, whilst cerium is absent from the group bearing its name. He also points out that the earths of this group contain 10 per cent. of thorium, a small quantity of didymium oxide and an earth (about 3 per cent. of the mineral) which the author considers to be new, if it is not the hypothetical terbium of Mosander. De la Fontaine of Chicago has confirmed the absence of cerium, and looks upon the new earth as terbia. The author thinks, nevertheless, that he has found a new earth, and that if terbia exists among the oxides of samarskite, it is contained in the yttria group.

Comparing the atomic weight of the supposed new earth with those of the oxides of cerium, lanthanum, or didymium determined by Marignac (O = 16) we have:—

New earth	109	(Smith).
Cerium oxide	110	(Marignac).
Lanthanum oxide	110	„
Didymium „	112	„

The new earth differs from those of the yttria group in its action with potassic sulphate, from cerium oxide by its solubility in very dilute HNO_3, from didymium oxide by its colour, from lanthanum oxide by its colour and the ease with which its salts are decomposed by heat.

The author has also devised a method for the separation of thorium, as follows: the freshly precipitated oxides are placed in a solution of potash or soda, and a current of chlorine is passed through the mixture when all the oxides are dissolved except those of cerium and thorium; as the samarskite contains no cerium, the residue consists merely of a white gelatinous precipitate of thorium oxide. J. M. T.

The supposed New Element Mosandrum. By J. L. Smith (*Compt. rend.*, **87**, 148—151).—This paper is occupied by a claim for the priority of the discovery of the earth indicated as X by Soret in his paper to the Academy. The author maintains to have found this earth in samarskite from North Carolina, and gives a minute account of its discovery and of his correspondence with De la Fontaine

and Marignac on the subject. Basing his remarks on his own work and the spectroscopic examination by Soret, he now has no hesitation in claiming mosandrum as a new element. J. M. T.

On the Discovery of a New Earth announced by J. L. Smith. By C. Marignac (*Compt. rend.*, **87**, 281—283).—In this paper Marignac points out the reasons leading him to the conclusion that Smith's "mosandrum" is identical with Mosander's "terbium;" whilst the earth provisionally designated X by Soret and the author, differs from the former in its absorption phenomena, although it shows many points of resemblance with an earth described by De la Fontaine of Chicago. J. M. T.

Magnetic Compounds having the Formula $\ddot{R}O.Fe_2O_3$. By K. List (*Deut. Chem. Ges. Ber.*, **11**, 1512—1516).—Lime water produces in a neutral solution of ferric chloride a brown precipitate, which is magnetic, and after ignition has the composition $CaO.Fe_2O_3$.

In a similar manner magnetic compounds of magnesia and baryta with ferric oxide can be obtained. The corresponding manganese, nickel, copper, and lead compounds are formed when soda is added to a solution containing ferric chloride and copper sulphate, &c., in their equivalent proportions. Magnetic compounds are also formed when sodium or potassium carbonate is fused with ferric oxide.

W. C. W.

Dissociation of Metallic Sulphides. By P. de Clermont and J. Frommel (*Compt. rend.*, **87**, 330, 332).—The decomposition which ensues on boiling certain sulphides with water is regarded by the authors as due to the dissociation of a previously formed hydrate of the sulphide. They point out that freshly precipitated sulphide of arsenic boiled with water gives rise to a more rapid evolution of sulphuretted hydrogen than the same sulphide does when it has previously been dried at 125°. But if this last is kept in contact for some hours with hot water in a closed vessel, it gives off sulphuretted hydrogen, when boiled in an open vessel, as rapidly as the freshly precipitated sulphide. On boiling sulphides with water in a vacuum, dissociation was observed to occur at the following temperatures: sulphide of arsenic, 22°; sulphide of iron, 56°; sulphide of antimony, 95°. The dissociation of arsenic sulphide presented certain peculiarities, which the authors believe to be due to the interference of the arsenious acid, which is one of the products of decomposition. The presence of this substance impedes the dissociation, by the formation, as they suppose, of an oxysulphide which undergoes dissociation more slowly.

Sulphide of arsenic, to which crystallised arsenious acid has been added, is dissociated more quickly than that to which arsenious acid obtained by the dissociation of the sulphide has been added. As arsenic pentasulphide on dissociation yields arsenious acid and not arsenic acid, the author doubts its existence as a definite chemical compound. R. R.

Mineralogical Chemistry.

The Fundamental Forms of Crystal Species. By A. Kenngott (*Jahrb. f. Min.*, 1878, 337—349).—It is of course an acknowledged rule, that in "derivation-forms" the axial relations of the primary or fundamental forms are modified by means of "derivation-coefficients," expressed as rational numbers. This assumption that the "derivation-coefficients are rational numbers," is open to a question, viz.: "Is it mathematically true that these coefficients are rational numbers?" C. F. Naumann, in his *Lehrbuch der reinen und augewandten Krystallographie*, Band I, says, "a very remarkable but thoroughly confirmed natural law for the derivation of forms is that the 'derivation-coefficients' are always rational numbers. This fundamental law must be considered as the result of all methods of derivation." The results of measurements of angles certainly always lead to rational numbers, but the above-mentioned law cannot be said to rest upon a proved mathematical basis. A second question may be asked, viz.: "Are the numbers expressing the lengths of the axes of the fundamental forms rational or irrational ones?" The author considers that they are irrational numbers (the numbers in the regular system belong neither to the rational or irrational, because the axial relations of the octohedron are expressed thus: 1 : 1 : 1, or by the formula $a : a : a$, thus merely showing that the axes are of equal length). In the quadratic and rhombic systems, however, the numbers which express the axial ratios of the primary pyramids must be irrational, for this reason, viz., if the "derivation-coefficients" are assumed to be rational numbers, the resulting axial ratios obtained expressed in rational numbers, lead inevitably to the derivation of the regular octohedron from a quadratic or rhombic pyramid. A third question may be asked, viz.: "Is the choice of a primary form a limited one, or in other words, do the values expressing the lengths of the axes of non-regular primary forms lie between certain limits?" The choice of a primary form in all the systems except the regular system, is optional, falling either upon one of the forms actually observed, or upon one obtained by calculation from the observed forms. It is often observed that a different primary form (in the same mineral species) is chosen by different observers, and also that the axial lengths obtained by calculation do not agree. The latter circumstance is due, in most instances, to the varying qualities of the goniometers used, and occasionally also to physical defects or abnormalities on the crystals themselves. In order to diminish the errors arising from such differing observations, the author suggests that crystallograpers should give the angles obtained by measurement or calculation of the primary form, and the resulting axial lengths of the primary forms, giving at the same time similar observations of other crystallographers for comparison; just as it is the rule to give the analyses of a substance by different chemists side by side. Naumann, in his *Lehrbuch* (already referred to), says for example in regard to the quadratic system, that every form whose parameters have the

finite relationship $a : 1 : 1$, can be chosen as a geometrical primary form; but as normal quadratic pyramids can alone be said to fulfil these conditions, they must therefore be chosen as primary forms. A pyramid P (of undetermined dimensions, with the parameter of the vertical axis standing to the parameter of a lateral axis in the relationship of "$a : 1$") is chosen as the primary form. Opinions are divided as to whether this relationship is a rational or irrational one; Hauy, Weiss, and Mohs expressing "a" as a square root, whilst Breithaupt has endeavoured to show that this number is rational, and is always a multiple of the coefficient $\frac{1}{7\,2\,0}$, the other lateral axis, or the intermediate axis being taken as unity. It is, however, immaterial for the independence of the quadratic system whether the one or the other of these opinions is the correct one, as the distinctive feature of the quadratic system is the contrast exhibited by one axis in regard to the other two axes, thus making a passage of quadratic forms into regular (tesseral) forms impossible.

This opinion of Naumann is at variance with that of the author, who has already stated above that the numbers cannot be rational ones, as the "derivation-coefficients" would in that case lead to the production of a regular octohedron, and not of a normal quadratic pyramid. As a proof of this opinion, the author points out that the axial relation $a : 1 : 1$ cannot be chosen in the derivation of the primary form of a "species," because the regular octohedron would probably occur in the series of normal pyramids obtained, and would with equal justice be chosen as the primary pyramid.

It is impossible for a quadratic species to exhibit the axial relation $a^2 : b^2 = 2 : 1$, as the faces of the primary pyramid P would intersect in a terminal edge at an angle of 101° 32′ 13″, and in a lateral edge at an angle of 126° 52′ 12″, consequently the pyramid P∞ would have equal lateral and terminal edge angles, and be a regular octohedron. In regard to the hexagonal system, it is evident, from its close similarity to the quadratic system, that the parameters of the lateral axes must differ in length from that of the vertical axis, although as Naumann states in his *Lehrbuch*, it is theoretically possible to have a primary hexagonal pyramid in which all the axes are of equal length. The author agrees with Naumann in considering such a form to be a purely theoretical one, because the close analogy existing between the quadratic and hexagonal systems in the characteristics of their forms, the laws relating to their hemihedry and tetartohedry and their physical properties, point to a similarity in their axial relations; whence it is safe to conclude that the length of the vertical axis of a hexagonal pyramid must differ from the lengths of its lateral axes. As a proof of this opinion, the author gives the following examples, viz.: "a normal hexagonal pyramid with the axial relation $a : b = 1 : 1$, would have an interfacial angle over a terminal edge of 135° 35′ 5″, and over a lateral edge of 98° 12′ 48″; the corresponding *rhombohedron* would have a terminal edge angle of 98° 12′ 48″, and the corresponding *trigonal pyramid* would have equal terminal and lateral edge angles, viz.: 98° 12′ 48″. The *diagonal pyramid* corresponding with this normal pyramid would have a terminal edge angle of 138° 35′ 25″, and a lateral edge angle of 90°, and the corresponding *diagonal rhom-*

bohedron would have a terminal edge angle of 104° 28′ 39″. Besides the above improbable axial relation (which would include every possible rational angle-relation obtained through rational "derivation coefficients"), the two axial relations $a^2 : b^2 = 3 : 2$ and $2 : 1$ are impossible, as will readily be seen from the following, viz.: "the axial relation $a^2 : b^2 = 3 : 2$ furnishes a normal hexagonal pyramid, having a terminal edge angle of 131° 48′ 36″, and a lateral edge angle of 109° 28′ 16″; the corresponding rhombohedron is the *cube*, and the corresponding normal trigonal pyramid has a terminal edge angle of 90° and a lateral edge angle of 109° 48′ 16″, whilst finally the diagonal hexagonal pyramid of the normal pyramid has a terminal edge angle of 134° 25′ 37″, and a lateral edge angle of 101° 32′ 13″, and the diagonal rhombohedron derived from the last-mentioned form has a terminal edge angle of 95° 44′ 21″. The axial relation $a^2 : b^2 = 2 : 1$ is equally impossible, as it also leads to the *cube* as a hexagonal form. From the above, therefore, it appears that a quadratic pyramid cannot exist having the same interfacial angle on a terminal edge as on a lateral edge, because it would in that case be a regular octohedron; and further, a rhombohedron cannot have the same angle on a terminal edge as on a lateral edge, because it would then be a cube. The author also considers it impossible for a normal hexagonal pyramid to have equal terminal and lateral edge angles. A normal hexagonal pyramid having the interfacial angle 126° 52′ 12″ on a terminal and lateral edge, requires the axial relation $a^2 : b^2 = 3 : 1$; its rhombohedron would have a terminal edge angle of 78° 27′ 47″, its trigonal pyramid the terminal edge angle 78° 27′ 47″, and lateral edge angle 126° 52′ 12″. The relative diagonal pyramid would have a terminal edge angle of 128° 40′ 56″, a lateral edge angle of 120°, and its rhombohedron (diagonal) would have a terminal edge angle of 82° 49′ 9″. A diagonal hexagonal pyramid having the same interfacial angle on its terminal and lateral edges, viz., 126° 52′ 12″, and whose diagonal rhombohedron has a terminal edge angle of 78° 27′ 47″, requires the axial relation $a^2 : b^2 = 4 : 1$, or $a : b = 2 : 1$. The relative normal hexagonal pyramid would have a terminal edge angle of 125° 22′ 36″, and a lateral edge angle of 133° 10′ 25″, its rhombohedron a terminal edge angle of 74° 44′ 33″, and its trigonal pyramid a terminal edge angle of 74° 44′ 33″, and a lateral edge angle of 133° 10′ 25″. The axial relation $a : b = 2 : 1$ would give the relative normal pyramid as a "derivation form" of the pyramid with the axial relation $a : b = 1 : 1$. If the latter form is found to be inadmissible, it follows that its "derivation forms" must also be inadmissible, and to this category belongs the pyramid 2P2, which has equal terminal and lateral edge angles. The axial relation $a^2 : b^2 = 6 : 1$, is also inadmissible, as will be seen from the following, viz.: the corresponding normal hexagonal pyramid would have a terminal edge angle of 123° 44′ 56″, and a lateral edge angle of 141° 3′ 27″, its rhombohedron would have a terminal edge angle of 70° 31′ 44″, and this form combined with 0R in a proper proportion would become a regular octohedron. The trigonal pyramid corresponding with the above-mentioned normal hexagonal pyramid would also be a regular octohedron. From the diagonal pyramid corresponding with the above-mentioned normal

pyramid, a diagonal rhombohedron is obtained, which in reality is a cube. It seems, therefore, from what has already been stated, that allowing primary forms to have rational "derivation coefficients" and irrational axial lengths, it still does not follow that any kind of irrational axial relation will furnish a primary form, because certain forms mentioned above are excluded. The author concludes by stating that the values of the axial relations of the possible primary forms must oscillate between certain limits. C. A. B.

Hetaerolite. A New Mineral. By G. Moore (*Jahrb. f. Min.*, 1878, 210—211).—This mineral occurs in botryoïdal radio-fibrous masses, always accompanying (ἑταιρος) chalkophanite in brown-iron ochre, at the Passaic zinc-mine, Sterling Hill, N. Jersey. Hetaerolite is black, has a semi-metallic lustre, a brownish-black streak, is infusible before the blowpipe, and evolves water on being heated in a closed tube. H. = 5 . Sp. gr. = 4·933. Its chemical composition corresponds with the formula $ZnO.MnO.MnO_2$, whence it appears to be a zinc-hausmannite. The chalkophanite is rhombohedral, and occurs in druses in thin laminæ or stalactitic aggregates. Colour bluish-black. Lustre metallic. H. = 2. Sp. gr. 3·907. Its chemical composition corresponds with the formula $2MnO_2 + (MnZn)O + 2H_2O$.

C. A. B.

The Origin of some Ores of Copper. By C. A. Burghardt (*Chem. News*, **37**, 215).—*Atacamite.*—The author considers this mineral to have had in most cases an aqueous and not an igneous origin, owing to the more common occurrence of globular and stalactitic atacamite; the crusts of atacamite in volcanic neighbourhoods (arising from the action of hydrochloric acid gas upon copper compounds) being comparatively scarce and insignificant in quantity. Natural atacamite is known to occur in three states of hydration, the chemical composition of each being as follows, viz.:—

(1.) *Atacamite from Algodon Bay, Bolivia* (von Bibra, *Jahresb.*, 1858, 740)—

Cu.	Cl.	O.	H_2O.	
59·25	16·11	12·51	12·13	= 100·00,

the formula corresponding with the above being $Cu_4O_3Cl_2 + 3H_2O$.

(2.) *Atacamite from Copiapo, Chili* (Field, *Journ. Chem. Soc.* [2], **3**, 193)—

Cu.	Cl.	O.	H_2O.	
56·38	14·95	10·78	17·89	= 100·00.

Formula = $Cu_8O_6Cl_4 + 9H_2O$ or $(Cu_4O_3Cl_2)_2 + 9H_2O$.

(3.) *Botallak Atacamite* (*a*) (Church, *Journ. Chem. Soc.* [2], **3**, 212)—

Cobija Atacamite (*b*) (Berthier, *Ann. des Mines.* [3], **7**, 542)—

	Cu.	Cl.	O.	H_2O.	
(*a.*)	52·90	14·76	10·49	22·45	= 100·00
(*b.*)	53·26	14·92	9·37	22·24	= 100·00

Formula = $Cu_4O_3Cl_2 + 6H_2O$.

Field (*Phil. Mag.* [4], **24**, 1862, 124) prepared an apple-green atacamite, corresponding with Berthier's atacamite from Cobija, by adding a solution of calcium hypochlorite to an excess of cupric sulphate. The author obtained (in addition to cuprite and chalcotrichite) very small quantities of a green substance resembling atacamite, by heating in one case cuprous chloride crystals with water in a sealed tube at a temperature ranging from 160—180°; in another case, by heating cuprous oxide with a strong solution of sodium chloride in a sealed tube at a temperature ranging from 150—180°. After numerous experiments, it was found that large quantities of atacamite were readily formed by simply covering cuprous oxide with a concentrated solution of sodium chloride, and exposing this mixture to the air. The cuprous oxide dissolves in the sodium chloride solution, forming a very concentrated solution of cuprous chloride, and the latter, on exposure to the air, rapidly decomposes, a green insoluble substance separating out. This substance was dried over calcium chloride until its weight was constant, then analysed, and found to have the following chemical composition—

Cu.	Cl.	O.	H_2O.	
56·25	14·29	10·95	18·51	= 100·00,

from which it will be seen that it agrees closely with the Copiapo atacamite. The first stage of the above reaction may be expressed by the following equation, viz. :—$3Cu_2Cl_2 + O_3 = CuCl_2.3CuO + 2CuCl_2$, the cupric oxychloride thus formed becoming eventually hydrated.

In a former paper (*Proc. Lit. Phil. Soc. Manchester*, **18**, 27—36) the author expressed an opinion that most of the ores of copper are the products of the decomposition of cuprous oxide; and the results detailed above seem to confirm this view, more especially as atacamite is nearly always intimately associated with cuprite, chalcedony, quartz, &c., occurring in diorite and syenite. C. A. B.

Uranium Pitchblende from Joachimsthal. By E. Reichardt (*Arch. Pharm.* [3], **13**, 130).—The sp. gr. of this mineral is 5·328; the colour brown-black with an ochrey coating; its composition is as follows:—

Si.	S.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	MnO.	Pb.
3·680	0·788	0·313	4·161	0·499	0·034	0·180	3·888

As.	Sb.	P_2O_5.	CuO.	U_2O_3.	Bi.	
0·261	0·068	0·072	0·578	83·918	trace	= 98·440

E. W. P.

Polydymite. By A. Kenngott (*Jahrb. f. Min.*, 1878, 183—185).—Laspeyres described this new mineral (*Jahrb. f. Min.*, 1877, 206), stating its composition to be as follows, viz. :—

Ni.	Co.	Fe.	S.	As.	Sb.	
53·508	0·606	3·844	40·270	1·041	0·508	= 99·777,

the formula corresponding with this analysis being $NiS.Ni_2S_3$, thus placing the mineral in the same class as musenite, which contains

both Ni and Co. The small amount of arsenic and antimony present points to a slight intermixture of gersdorffite and ullmannite with the polydymite. Further, Laspeyres was of opinion that the nickel-bismuth-glance (saynite, grünauite) analysed by von Kobell, was a mixture of polydymite with bismuthine, galena, and chalcopyrites (copper-pyrites), and this opinion is considered by Kenngott to be well founded, as he obtained the formnla $NiS.Ni_2S_3$ on deducting the several percentages of bismuthine, galena, and chalcopyrites obtained by calculation from von Kobell's analysis. C. A. B.

Yellow Dolomite from Bleiberg. By V. von Zepharovich (*Jahrb. f. Min.*, 1878, 315).—This dolomite occurs fine-grained and massive, with a sulphur-yellow to brownish-yellow colour, and often enclosing yellowish-brown zinc-blende. The yellow colour of the dolomite is most intense in the neighbourhood of the enclosed zinc-blende, Small drusy cavities occur in the dolomite containing zinc-blende, which are filled with hemimorphite crystals, accompanied by yellowish-white calcite rhombohedrons. A microscopical examination showed the dolomite to be homogeneous (excluding of course the zinc-blende enclosures). Sp. gr. = 2·87. An analysis showed it to have the following composition, viz. :—

$CaCO_3$.	$MgCO_3$.	$ZnCO_3$.	$FeCO_3$.	ZnS.	CdS.	FeS_2.	SiO_2.
79·48	16·71	2·42	0·30	0·31	0·25	0·08	0·03 = 99·58.

The formula corresponding nearly with the above is $4CaCO_3 + MgCO_3$. The yellow colour is due to the presence of cadmium sulphide. C. A. B.

A Boron Mineral from Chili. By E. Reichardt (*Arch. Pharm.* [3], **13**, 131).—In the Chili saltpetre beds, together with calcium borate and boronatrocalcite, a mineral is found in powder having the composition—

Water	18·107
Sand and clay	15·056
Silica	0·070
Ferric oxide and alumina	0·840
Lime	0·727
Magnesium chloride	1·109
Sodium chloride	3·763
Potassium chloride	1·310
Calcium sulphate	32·247
Sodium biborate	26·611
	99·840

E. W. P.

Deposits of Calcium Phosphate in the Vosges. By P. Guyot (*Compt. rend.*, **87**, 333). At Damblain and Blevaincourt, in the Vosges, are found kidney-shaped masses of calcium phosphate from 2 to 10 centimeters in dimeter. A sample from Damblain yielded 76·99 per cent. of tribasic phosphate; one from Blevaincourt 77·74 per cent. R. R.

New Minerals from Fairfield Co., Connecticut. By G. J. Brush and E. S. Dana. First Paper (*Amer. Jour. Sci.* [3], **16**, 33—46).—These minerals were found in a vein of albitic granite, associated with a large number of others; six new species were identified. Those described in the following paper occur associated in the most intimate manner, although distinct crystals can be obtained.

Eosphorite occurs in prismatic crystals, often of considerable size, more generally massive. Hardness = 5. Sp. gr. (mean) = 3·134. Lustre vitreous to subresinous; of the massive mineral often greasy. Colour of the crystals pink, yellow, and grey; of the massive mineral pale pink, greyish, bluish-, and yellowish-white and white, sometimes greenish, owing to admixture of dickinsonite. Transparent to translucent. Streak nearly white. Fracture uneven to subconchoidal.

The crystals are prismatic in habit, showing but one terminated extremity, and belong to the orthorhombic system. The surfaces of the crystals are often covered with drusy quartz and with apatite; the prismatic planes almost always, and the pyramidal planes very often, are finely striated, giving rise to rounded barrel-shaped crystals. The crystals are closely analogous to those of childrenite. Observed planes: $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, ∞P, $\infty\breve{P}2$, P, $\frac{3}{2}\breve{P}\frac{3}{2}$, $2\breve{P}2$. Axial ratio, $\breve{a} : \breve{b} : c$ (vert.) = 1 : 1·28732 : 0·66299. Angle, P : P (in the terminal edges) = 61° 1′ 54″; P : P (in the basal edges) = 46° 27′ 45″; ∞P : ∞P = 75° 36′; $\infty\breve{P}\infty$: ∞P = 52° 12′ : ∞P : P = 49° 55′.

The three axes of elasticity coincide with the crystalline axes; the optical axes lie in the macrodiagonal section or plane of cleavage. The axial angle is (approximately) 2E = 54° 30′ (for red rays) and 60° 30′ (blue rays). The dispersion of the axes is strong $\nu > \rho$; the character of the double refraction is negative. A parallelopiped, cut with its edges parallel to the three crystalline axes, showed a distinct trichroism. The mean composition is as follows:—

P_2O_5.	Al_2O_3.	FeO.	MnO.	CaO.	Na_2O.	H_2O.
31·05	22·19	7·40	23·51	0·54	0·33	15·60 = 100·62,

corresponding with the formula $R_2Al_2P_2O_{10}.4H_2O$, or $Al_2P_2O_8 + 2H_2RO_2$ + 2Aq. Eosphorite differs from childrenite in containing a larger proportion of manganese and a smaller proportion of iron. It is essentially a phosphate of aluminium and manganese, childrenite being a phosphate of aluminium and iron.

In a closed tube eosphorite decrepitates, whitens, gives off water, and turns black, grey, and then brown with metallic lustre, and becomes magnetic. Before the blowpipe, it cracks open, colours the flame pale green, and fuses to a black magnetic mass. It dissolves completely in the ordinary fluxes, giving iron and manganese reactions. It is soluble in hydrochloric and nitric acids.

Triploidite.—This mineral occurs in crystalline aggregates, which are parallel-fibrous to columnar or divergent, sometimes confusedly fibrous to nearly massive. Occasionally distinct crystals are found imbedded in quartz, from which they cannot be separated without breaking into small pieces; rarely crystals may be found projecting into cavities in the massive mineral.

The hardness of triploidite is 4·5—5°; sp. gr. 3·697. Lustre vitreous to greasy-adamantine; colour yellowish- to reddish-brown; crystals topaz- to wine-yellow and sometimes hyacinth-red. Streak nearly white; transparent to translucent; fracture sub-conchoïdal.

The crystals belong to the monoclinic system and are homeomorphous with wagnerite; they are much striated and occasionally exhibit false planes. Of the two axes of elasticity which lie in the plane of symmetry, one nearly coincides with the vertical axis, the other is almost normal to the orthopinacoïd. The mean chemical composition is as follows:—

P_2O_5.	FeO.	MnO.	CaO.	H_2O.
32·11	14·88	48·45	0·33	4·08 = 99·85,

leading to the formula $R_4P_2O_9.H_2O$, or $R_3P_2O_8.H_2RO_2$, where R = Mn : Fe = 3 : 1. Triploidite is therefore related in composition to libethenite, olivenite, and lazulite, none of which, however, have similar crystalline forms. In crystalline form it resembles wagnerite, which again is analogous to triplite in composition, thus showing a relation between triplite and triploidite. Observed planes: 0P, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, ∞P, $\breve{P}\infty$, $2\breve{P}2$. Axial ratio, $a : b : c$ (vert.) = 1 : 0·53846 : 0·80367. Angle, 0P : $\infty\breve{P}\infty$ = 54° 48′; $\infty\breve{P}\infty$: ∞P = 60° 27′; $\infty\breve{P}\infty$: 0P = 71° 46′; ∞P : ∞P = 59° 6′; $\infty\breve{P}\infty$: 0P = 71° 55′.

In a closed tube, triploidite gives off water, turns black, and becomes magnetic. Fuses quietly in the naked flame, and before the blowpipe in the forceps colours the flame green. Dissolves in the fluxes, giving reactions for manganese and iron. Soluble in acids. The darkest specimens contain the most iron. C. W. W.

Thaumasite, a new Mineral Species. By Nordenskiöld (*Compt. rend.*, **87**, 313).—This substance, obtained from a mine at Areskustan, has been analysed under the author's direction, with results leading to the formula $CaSiO_3.CaSO_4.CaCO_3 + 7H_2O$.

R. R.

Some Minerals from Laangban. By A. E. Nordenskiöld (*Jahrb. f. Min.*, 1878, 206—209).—*Atopite* (ἄτοπος = unusual), *a new mineral*, crystallises in predominating regular octohedrons, in combination with the cube and rhombic dodecahedron and indications of the trapezohedron and tetrakis-hexahedron. Yellowish-brown to resin-brown, resinous lustre, semi-transparent. H. = 5·6 to 6. Sp. gr. = 5·03. On heating it in the oxidising flame before the blowpipe, no change is observable; it gives a deposit on charcoal and leaves an infusible slag-like residue after the volatilisation of all the antimony; gives a faint trace of Mn on treating it with carbonate of soda and nitrate of potassium. Soluble in microcosmic salt without separation of silica, the bead being yellow when hot and colourless when cold; insoluble in acids. Chemical composition as follows, viz.:—

Sb_2O_5.	CaO.	FeO.	MnO.	K_2O.	Na_2O.
72·61	17·85	2·79	1·53	0·86	4·40 = 100·04.

Formula $2RO.Sb_2O_5$. From the above it would seem that atopite resembles very closely monimolite and romeite, differing however from the former in the absence of lead and a higher amount of antimonic oxide, and from the latter in a double amount of bases, the crystal form, and the different state of oxidation of the antimony present. Atopite occurs mostly disseminated in very fine veins and deposits of hedyphane, which penetrates rhodonite. *Monimolite* is found at Laangban in brown crystals and grains in calcite-druses enclosed in rhodonite and tephroide.

Ekdemite (εκδημος = absent, foreign), a new mineral, coarse-crystalline, foliated, monoaxial, with a distinct basal cleavage. Light yellow with a greenish tinge, translucent in thin splinters, resinous lustre on broken surfaces, on cleavage-planes a strong vitreous lustre. H. = 2·5—3. Sp. gr. 7·14. Brittle. Decrepitates in a closed tube and crumbles to powder, a yellow fused mass separating out with ease, and at the same time a sublimate of lead chloride. Heated on charcoal it furnishes a lead-bead and a deposit of lead oxide and chloride. Arsenic is also present. Soluble in nitric acid and warm hydrochloric acid. An analysis of this mineral proved it to have the following composition, viz.:—

PbO.	Pb.	Cl.	As_2O_3.
58·25	23·39	8·00	10·60 = 100·24.

The formula corresponding with the chemical composition is $5PbO\ As_2O_3,2PbCl_2$.

Hydrocerussite.—Hydrated carbonate of lead surrounding native lead. White by transmitted light; colourless, quadratic laminæ, having a very distinct foliation. Decrepitates in the closed tube and becomes yellowish-brown. Yields a lead-bead on charcoal. Soluble in acids with efflorescence. Rather soft. The author considers its composition to correspond with the formula $2PbOCO_2,H_2O$.

Hyalotekite (ὑαλος = glass, and τήλειν = melt, fuse).—A new mineral. Occurs in coarse crystalline masses, exhibiting two directions of foliation which intersect each other at an angle of about 90°. H. = 5 to 5·5. Sp. gr. = 3·81. Vitreous to resinous lustre; white to pearl-grey; semi-translucent; brittle; fuses easily before the blowpipe to a clear colourless bead, which becomes black on heating it in the reducing flame owing to the reduction of lead. Gives the reaction for silica with microcosmic salt, and a lead-bead on reducing a portion of the mineral with sodium carbonate, also a yellow deposit when heated alone on charcoal. Insoluble in hydrochloric and sulphuric acids. An incomplete analysis furnished the following results, viz.:—

SiO_2.	PbO.	BaO.	CaO.	Loss on ignition Al_2O_3, K_2O, &c.
39·62	25·30	20·66	7·00	0·82

Hyalotekite is accompanied by hedyphane and schefferite, and generally resembles a greyish-white felspar.

Ganomolite (γάνωμα = lustre).—A new mineral. Occurs massive, accompanied by tephroite, which it closely resembles; in fact, it is often necessary to resort to the blowpipe in order to distinguish

between them. Cleavage indistinct. Strongly double refracting, colourless, white to greyish-white, strong resinous lustre, translucent. H. = 4. Sp. gr. 4·98. Fuses before the blowpipe to a clear bead, which become black on the surface in the reducing flame. Gives a lead-bead and a yellow deposit. Easily soluble in nitric acid, with separation of gelatinous silica. An analysis gave the following results, viz. :—

SiO_2.	PbO.	MnO.	CaO.	MgO.	Alkalis and loss.
34·55	34·89	20·01	4·89	3·68	1·86.

Jacobsite.—This mineral which is strongly magnetic, has the following chemical composition, viz. :—

Fe_2O_3.	Mn_2O_3.	MnO.	MgO.	CaO.	P_2O_5.	Pb.	Insoluble residue.
58·39	6·96	29·93	1·68	0·40	0·06	1·22	2·17 = 100·81.

The formula corresponding with the above is $MnO(Fe_2O_3Mn_2O_3)$.

C. A. B.

Magnetite from Monte Mulatto, South Tyrol. By V. von Zepharovich (*Jahrb. f. Min.*, 1878, 310).—The crystals clothe drusy hollows in a tier-like mass of magnetite. Their size is sometimes 5 to 8 mm. They exhibit the combination $\infty O.5O\frac{5}{3}$. 303.O. Similar forms were observed by von Kokscharow, occurring on the magnetite of Achmatowsk, and by Struve on the Albanese magnetite.

C. A. B.

The Mirabilite from Aussee. By V. von Zepharovich (*Jahrb. f. Min.*, 1878, 314).—Some crystals of mirabilite from the salt mines of Aussee exhibited the following forms in combination, viz. :—
0P, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, $-\frac{1}{2}\breve{P}\infty$, $\frac{1}{2}P\infty$, $\breve{P}\infty$, $\breve{P}\infty$, $2\breve{P}\infty$, ∞P, $-$P, P, $\frac{1}{2}$P, $-\frac{1}{2}$P, -2P; the latter two forms being new to this mineral. The orthopinacoïd generally predominates, whilst the faces of the clinodiagonal zone occur only in a secondary position. Most of the crystals (particularly the largest) exhibit an unusual "habit," on account of an abnormal vertical development, their height varying from 7 to 10 cm., and their width from 3 to $2\frac{1}{2}$ cm., and they are generally terminated by 0P or pyramids. Short tabular crystals through $\infty\breve{P}\infty$ are comparatively rare. C. A. B.

The Sericite Rocks of the Taunus. By A. Wichmann (*Jahrb. f. Min.*, 1878, 264—275).—The author shows plainly that the conclusions of K. A. Lossen (*Zeits. Deut. Geol. Ges.*, 1867, 1877) are erroneous. Judging from the presence of a certain percentage of soda in the Taunus rocks, Lossen endeavours to prove albite as a constituent; but a microscopical examination of these rocks proved the absence of unsymmetrical felspar. Albite is observed to occur only in bands or streaks, but never as a rock-constituent, and the percentage of soda is referable to a sodium-aluminium silicate, which constitutes the groundmass of the slatey-rocks of the Taunus. C. A. B.

Examination of Lithia-Mica from Paris (Maine), Rozena, and Zinnwald. By F. Berwerth (*Jahrb. f. Min.*, 1878, 316).—

The author analysed the lithia-mica from the above localities, taking perfectly pure material furnished by Tschermak for the purpose.

A. Lithia-mica, from Paris (Maine); B. Ditto from Rozena; C. Ditto from Zinnwald.

	P_2O_5.	Fl.	SiO_2.	Al_2O_3.	FeO_3.	FeO.	MnO.	K_2O.
A....	—	5·15	50·39	28·19	—	—	trace	12·34
B....	0·05	7·88	50·98	27·80	—	0·95	trace	10·78
C....	6·08	7·94	45·87	22·50	0·66	11·61	1·75	10·46

				Less oxygen		
Na_2O.	Li_2O.	H_2O.		equivalent to fluorine.		
—	5·08	2·36	= 103·51	— 2·17	=	101·34
—	5·88	0·96	= 104·38	— 3·32	=	101·06
0·42	3·28	0·91	= 105·48	— 3·34	=	102·14

Rubidium and cæsium were detected by the spectroscope. The sp. gr. of the three lithia-micas A, B, C, were 2·8546, 2·834, and 2·9715 respectively. C. A. B.

The Crystal-System of Potash Mica. By M. Bauer (*Jahrb. f. Min.*, 1878, 310).—The author determined the angle which the plane of the axes forms with the basal plane, and obtained values which coincide with those obtained by Tschermak. The results were as follows, viz.:—(1.) Potash mica is optically monosymmetrical. (2.) The plane of the optical axes is perpendicular to the plane of symmetry, and the bisectrix is situated in the latter. (3.) The angle formed by the *apparent* bisectrix with the basal plane = 87° 5′, that formed by the *apparent* bisectrix with the normal to the basal plane = 2° 55′, the true angles being 88° 18′ and 1° 42′ respectively. The direction of the bisectrix could not be determined. (4.) The angle of the *apparent* optical axes is 64° 14′, the angle of the *true* axes being 40° 21′. (5.) The *apparent* angle formed by the optical axes with the normal to the basal plane = 32° 14′, the *true* angle being 20° 15′. C. A. B.

Occurrence of Disthene in Central Africa. By T. Liebisch (*Jahrb. f. Min.*, 1878, 313—314).—Disthene is found in the mica-slate of the Baginse Mountains, in East Niam-Niam-Land, enclosed in quartz crystals, and accompanied by biotite and muscovite. The disthene crystals are asparagus-green in colour. There are numerous biotite laminæ interpolated in the disthene crystals, parallel to the face $\infty P\bar{\infty}$. The forms observed were $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, $\infty P'$, $\infty'P$, $\infty P'\bar{2}$; the terminal plane was not observed. Some of the crystals were twins, according to the law "the twin axis the normal to the macropinacoïd."

C. A. B.

Duporthite, a New Asbestiform Mineral. By J. Collins (*Min. Mag.*, **7**, 226).—This mineral occurs in fibrous masses, filling clefts in serpentine. H. = 2; sp. gr. = 2·78. Greenish to brownish-grey; silky lustre; flexible; heated in a matrass, it evolves water; and fine fibres fuse before the blowpipe to a black glass. Insoluble in hydrochloric acid. An analysis furnished the following results, viz.:—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	H_2O.	Hygroscopic H_2O.	
49·21	27·26	6·20	11·14	0·39	0·49	3·90	0·68	= 99·27.

Considering part of the water to be water of constitution, the formula derived from the analysis is $3(Al_2O_3SiO_2)5(\frac{3}{5}Mg\frac{1}{5}Fe\frac{1}{5}H_2)O + SiO_2$. The mineral approaches nearest to the neolite of Dana. The author named it from the place where it was found, viz., Duporth, near St. Austell, Cornwall. C. A. B.

The Stone of the "Julius Column," the Lavez Rock in the Upper Engadine, and the Sericite-gneiss in the Bündener Alps. By C. W. Gümbel (*Jahrb. f. Min.*, 1878, 296—300).—The Julius Column, which dates from the time of the Romans, is remarkable for the freshness of its colour and the total absence of any signs of weathering. The author examined chemically and microscopically some small fragments which had probably been detached from the column by the action of frost. The stone is rather soft, greasy to the touch, of a greenish colour, and a scaly granular structure, which latter peculiarity arises from the occurrence of thin, cleavable, elastic laminæ in isolated groups. There can be no doubt that this rock is a "potstone." A considerable amount of the rock is soluble in hydrochloric acid, the soluble portion consisting of an impure magnesite (containing calcium and iron carbonates), and a magnesium mineral which plays the part of a cement in the rock. An analysis gave the following results:—

	SiO_2	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	MgO.	CaO.
Complete analysis	46·312	2·105	10·134	trace	36·161	0·251
Portion soluble in HCl ..	25·15	2·09	14·90	,,	44·59	—
Portion insoluble in HCl	57·96	1·90	5·80	,,	30·85	1·14

	K_2O.	Na_2O.	$CaCO_3$.	$MgCO_3$.	H_2O.	
Complete analysis	0·050	0·920	1·500	4·300	1·202	= 100·935
Portion soluble in HCl ..	—	—	3·36	7·48	2·09	= 99·66
Portion insoluble in HCl	0·67	2·21	—	—	—	= 100·53

The iron was mostly present as ferrous oxide; there were also traces of titanic acid present. On examining the above results, it would appear that a serpentine-like mineral must be present in the rock, as the amount of silica in the portion soluble in hydrochloric acid is very low in comparison with the amount of magnesia. Magnetic iron was also ascertained to be present in the powdered rock. The portion insoluble in the acid was principally talc, intermingled in varying amounts with chlorite, tremolite, and a sodium-felspar. A slight trace of chromium also points to the presence of chromite. The microscopical examination of thin sections of the rock supported the conclusions drawn from the chemical analysis, as it was found to consist of (1) fine-fibrous, green portions of varying intensity of colour; (2) of broad indented non-fibrous portions. Some of the fibrous portions exhibited distinct dichroïsm, and were probably chlorite and tremolite, whilst some small, non-fibrous, colourless portions exhibited in polarised light the peculiar reddish shimmer which

characterises the carbonates. Some colourless portions full of parallel rifts were also observed, pointing to the presence of talc. Between the fibres, and often on the edges of the colourless laminæ, a powder having a metallic lustre was observed, which was no doubt magnetite. There were also here and there isolated, roundish-brown granules (putzen), which externally pass almost imperceptibly into the "groundmass" surrounding them, but towards their interior exhibit the reticulation characteristic of serpentine, so that it may be inferred that these granules were orginally olivine. On examining a thin section after treatment with hydrochloric acid, it was found to contain isolated cavities, thus pointing out the position of the carbonate portions. On treating a section with caustic potash (after the hydrochloric acid treatment), it disintegrates into a mass of greenish needles and laminæ. From the above examination, the author considers the rock to be held together by a decomposible substance, such as serpentine, brucite, and a chloritic mineral.

Potstone of Chiavenna.—For comparison with the rock just described, sections were prepared of the Chiavenna potstone. This rock resembles closely that of the Julius Column, but the brown, roundish granules are commoner, and consist on their external surface of a homogeneous fibrous mass, whilst the central portion consists of a cloudy, dark-coloured substance, filled with a great quantity of very fine black dust, and dark needles running in all directions.

In order to ascertain from whence the Romans obtained the stone of the Julius Column, the author examined some specimens closely resembling it, which he found in numerous quarries at Pontresina in the Upper Engadine. An analysis furnished the following results, viz.:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	MnO.	CaO.	MgO.
Complete analysis	35·90	0·89	11·30	0·23	trace	0·67	24·14
Portion soluble in HCl ..	28·77	trace	11·82	0·25	—	trace	21·67
Portion insoluble in HCl .	54·80	1·50	7·52	trace	—	2·33	30·50
Potstone of Chiavenna (Delesse).....	36·57	—	5·85	—	—	1·44	35·39

	K_2O.	Na_2O.	$FeCO_3$.	$CaCO_3$.	$MgCO_3$.	H_2O.
Complete analysis.....	0·23	1·09	1·20	2·30	17·85	6·10=101·68
Portion soluble in HCl .	—	—	1·70	3·23	25·07	8·42=100·91
Portion insoluble in HCl	0·80	3·78	—	—	—	— =101·23
Potstone of Chiavenna (Delesse).....	—	—		14·03		4·97=100·00

The excess in the complete analysis and the portion insoluble in hydrochloric acid is due to the iron being determined as ferric oxide, whereas it exists in the rock mostly in the ferrous state. The Pontresina rock contains a larger amount of carbonates than the rock of the Julius Column, but leaving this out, there is a very close analogy between them, and the Chiavenna rock belongs also to the same group. A microscopical examination proved the identity of the rock of the Julius Column with that of Pontresina: hence it may be safely

inferred that the Romans used the latter rock for the erection of the column. C. A. B.

The Granite-porphyry of Beucha, near Leipzig. By E. Kalkowsky (*Jahrb. f. Min.*, 1878, 276—286).—Zirkel was the first to make the important discovery that the granite-porphyry from Beucha contained "glass-enclosures" (*Micros. Besch. d. Min. & Gest.*, Leipzig, 1873).—This was afterwards confirmed by Rosenbusch (*Micros. Phys.*, 1877, Bd. II, 8). Zirkel describes the granite-porphyry from Beucha and Altenberg thus:—"It is an aggregate of crystalline minerals, amongst which quartz predominates over felspar. The microscopical quartz of the ground-mass is nearly always in sharply defined crystals, which yield rhombic or hexagonal sections. These crystals are so intimately intergrown with each other and the rectangular cloudy orthoclase crystals, that no microfelsitic substance intervenes between them. The larger quartz-crystals are characterised further by numerous fine "glass-enclosures," often of a dihexahedral form, and this is the more remarkable as the rock is of a crystalline constitution throughout, and such enclosures are peculiar to rocks in which a portion of the magma is amorphous. There are also movable liquid globules observed occasionally in the quartz, and the clear parts of the orthoclase crystals contain numerous rectangular "glass-enclosures," the latter occurrence being extremely rare in quartz-porphyry, but common in granite. The rock contains also hornblende and chlorite, the latter mineral being in all probability a secondary product of the decomposition of the former.

Baranowski considered the green substances of this rock to be augite, and not hornblende; and allowing the correctness of this conclusion, the granite-porphyry of Beucha is most closely related to the augitic felsite-porphyry of the neighbourhood of Leipzig described by Kalkowsky (*Zeits. Deut. Geol. Ges.*, **26**, 1874). Augite-felsite-porphyry is a coal-black to grey rock, having a true felsite porphyry habit, with porphyritic quartz, felspar, and small black augite crystals. The dark colour is due to the great quantity of magnetic and titanic iron. Biotite constantly accompanies the augite, and apatite and iron-pyrites are accessory constituents; the ground-mass is perfectly granular, the grains diminishing sometimes to a scarcely recognisable size. The acid-rocks of this series "weather" easily, the felspar becoming more clouded and the augite fibrous. The granite-porphyry of Beucha (and the almost identical granite-porphyry of the banks of the Mulden from Trebsen to Wurzen) is connected in a threefold manner with the above-mentioned augite-felsite-porphyry, viz.:—(1.) Its geological occurrence in the immediate neighbourhood of the augite-felsite-porphyry. (2.) The granite-porphyry of Beucha is mostly of a reddish tint, owing to the presence of reddish orthoclase, but there are also many degrees of colour observed, viz., from light-red to dark-red, violet, grey-violet, blackish-grey, greyish-black to black. The porphyritic habit is caused by the occurrence of large red-orthoclase crystals and white plagioclase; whilst the large porphyritic quartz-crystals disappear entirely. On the northern perpendicular wall of the quarry, the greyish-black variety occurs, con-

taining large colourless felspar crystals, which variety is scarcely distinguishable from the true augite-felsite-porphyry. There can be no doubt that it is the final member of a series of these rocks distinguishable by colour alone (more compact varieties being pure black), and it gradually passes into the rock containing numerous red orthoclase crystals. (3.) The third bond of union between the two rocks is that augite is common to both. Fresh strongly pleochroitic augite was found by the author in two preparations only, it being generally fibrous, as in augite-felsite-porphyry. All specimens exhibiting a reddish tinge contained no fresh augite, but pseudomorphs of chlorite, quartz, and a mineral resembling epidote. No hornblende could be detected. The secondary quartz in the centre of the pseudomorphs is penetrated by a mass of pores, badly formed and sometimes radiating. Small druses in the chlorite contain a light-yellow columnar mineral, which may be epidote. All the quartzes contain fluid enclosures, but not in any great number. The large porphyritic quartz crystals contain numerous glass enclosures; one crystal 0·1 mm. in diameter contained five glass enclosures, whilst another crystal contained a glass enclosure which was $\frac{1}{4}$ to $\frac{1}{3}$ of its own bulk. The orthoclase crystals owe their colour to hydrated ferric oxide, which has separated out. All the plagioclases exhibit a polysynthetical twin-formation. Zirkel observed that orthoclase does not decompose regularly, but that in the centre of the crystal a pellucid adular-like kernel remains, surrounded by clouded orthoclase. The author found that *all porphyritic orthoclase* exhibits a perthite-like intergrowth of monosymmetrical orthoclase, with a polysynthetically twinned plagioclase, most probably albite. Further, he observed that the orthoclase substance undergoes most readily a molecular change where the small albite crystals occur, the adular-like portions being completely free from interpolated asymmetrical felspars. From the above it appears that an interpolation of unsymmetrical felspars in orthoclase-crystals causes them to be more susceptible to atmospheric action. Most of the porphyritic felspar-crystals are well and sharply defined, and those having a roundish form are often surrounded by a row of small quartz crystals, attached to each other like pearls in a necklace. The accessory minerals of the Beucha granite-porphyry are biotite, magnetite, titanic iron, apatite, and garnet. Biotite was most common in the greyish-black variety, being rare in the reddish variety. The apatite occurs generally in the chlorite-pseudomorphs, but it is also found in the ground-mass between the quartz and felspar. Red garnet occurs seldom, and in small grains. The ground-mass of the Beucha granite-porphyry is a crystalline granular mixture of quartz and felspar, with secondary chlorite, oxides of iron, and some apatite, but not a trace of microfelsitic substance was detected on any of the preparations. It is a curious fact that the diameters of the quartz and felspar crystals of the ground-mass are about the same, viz., from 0·07 to 0·10 mm. The author concludes from his own observations, and those of other mineralogists, that the augite-granite-porphyry of Beucha must henceforth be classed geologically with the felsite-porphyries, and not with the granites. C. A. B.

Mineralogical-petrographical Notes on the Granite-porphyry of Lower Silesia. By T. Liebisch (*Jahrb. f. Min.*, 1878, 311—313).—The granite-porphyry of the Riesengebirge is composed of the following minerals: quartz, orthoclase, plagioclase, biotite, potash-mica, hornblende, augite, magnetite, apatite, and orthite. The quartz occurs in well developed, mostly pyramidal crystals (occasionally exhibiting narrow prism-faces), with rounded edges, and often enclosing movable globules of liquid, but no microlites. The orthoclase crystals often occur colourless and transparent, exhibiting an adular-like shimmer. They are occasionally colourless in the interior only, whilst externally they have a reddish colour. Some of them are white, with a zonal structure. The crystalline form varies in different localities; one form observed on orthoclase crystals from Hermsdorf was ∞P. $0P.2\breve{P}\infty$. Twins according to the Carlsbad law are very common. The size of these crystals varies from a few millimeters to several centimeters in the direction of the axis *c*. Enclosures of biotite and quartz crystals are very common in the orthoclase crystals, although many of the colourless crystals are almost homogeneous. The orthoclase of the granite-porphyry of the Altarstein (the southernmost rock of the Gräbersteine) is penetrated by perthitic plagioclase, that between Kirche, Wang, and Brückenberg being enclosed by plagioclase. Interpolations of isolated plagioclase crystals are often observed in the orthoclase of the Riesengebirge granites, occurring parallel with the second cleavage plane of both felspars. In some localities, a considerable decomposition of the orthoclase is observable, the product being greenish or yellowish mica. The plagioclase crystals vary from 1 mm. to 3 cm. in size, and are generally white or yellowish, seldom red. Double twins occur at Hermsdorf and other localities, the twin axis being "the normal to the brachypinacoid" for the twin, and the twin axis being "the normal to the vertical axis in the brachydiagonal" for the double twin. The plagioclase of the granite-porphyry from the quarry between Erdmannsdorf and Stonsdorf exhibits a zonal structure. The plagioclase "weathers" much more easily than the orthoclase, the product being a light-coloured mica. Sometimes a greenish mica occurs in radiating divergent sheaves, which exhibit in polarised light a black "interference-cross," and also occasionally a reddish-brown substance resembling pyknotrope. Numerous veins of quartz penetrate the granite-porphyry at all localities. The biotite occurs in well-defined tabular or prismatic crystals of a greenish-black or black colour, and exhibiting in section a distinct hexagonal outline. Sections made parallel to the axis C are transparent and of a green colour on their edges, whilst internally the colour is brown, and some sections exhibit alternately green and brown transparent laminæ. Hornblende occurs but sparingly as a constituent of the granite-porphyry, the principal locality being westward between Erdmannsdorf and Stonsdorf. At Erdmannsdorf greenish-black augite occurs as an accessory constituent, and at the same place and at Lomnitz orthite occurs as an accessory constituent in acicular crystals $\frac{1}{2}$ to 1 cm. in length, with an orthodiagonal development. The ground-mass of all the Riesengebirge granite-porphyries is massive, and seldom preponderates over the crystallised rock-constituents. It is grey to reddish-

brown in colour, except in the "salbands," when it is black. Quartz, orthoclase, plagioclase, mica, &c., constitute the ground-mass, which is microcrystalline and coarse-grained. The so-called "pseudosphærolites" of Rosenbusch occur in great beauty, 0·2 to 0·4 mm. in diameter, in a vein between Erdmannsdorf and Stonsdorf, and in the granite-porphyry of Buschvorwerk. The difference between the constitution of a rock from the middle of a vein and from a salband is very marked in a granite-porphyry vein in a quarry between Erdmannsdorf and Stonsdorf. The granite-porphyry from the centre of the vein contains in the grey ground-mass large white and greenish-white orthoclase and plagioclase crystals, grey quartz crystals, and greenish-black biotite. These crystals diminish in size as their distance from the centre of the vein increases. The salband rock contains in the massive blackish ground-mass only very small orthoclase, plagioclase, quartz, and black biotite crystals. The orthoclase and plagioclase crystals, however, were penetrated by innumerable small biotite laminæ, and between the latter was a double refracting cryptocrystalline mineral, which could not further be studied. On account of the band-like arrangement of the felspar and biotite crystals of the ground-mass around the isolated crystalline constituents of the rock, the author considers that a fluid structure is indicated.

C. A. B.

Occurrence of Dioptase on Chrysocolla, from Peru. By C. A. Burghardt (*Chem. News*, **37**, 223).—The author examined some specimens received from Mr. W. M. Hutchings, of Birkenhead, which the latter thought to contain dioptase. The exact locality of the mine is unknown, but the chrysocolla was shipped from the port of Pisco, Peru. The specimens examined exhibited certain cavities here and there, which appeared to have been eaten out of the mass by the action of some powerful solvent. These cavities were divided into numerous cells by the intersection of thin portions of chrysocolla substance, and upon these partition walls were attached particularly fine sheaves and bundles of emerald-green transparent crystals. These crystals were so extremely small that it was almost impossible to make accurate measurements, but the forms characteristic of dioptase, viz., ∞P2, -2R, were well defined. No other forms were observed. Sometimes numerous fine acicular sub-individuals growing parallel to each other built up a large individual. Carefully picked crystals gave all the blowpipe reactions for dioptase. The dioptase crystals were associated with colourless quartz crystals, the forms $+$R. $-$R. on the latter being in equilibrium. This is the first instance observed of the occurrence of dioptase in Peru. Maskelyne (*Chem. News*, **24**, 99) mentions some specimens of dioptase in the British Museum, one of which is said to have come from the Rosario Mine, Chili, another (associated with quartz and eisenkiesel) from the Mina del Limbo del Salado, Copiapo, Chili. Only one of these specimens is associated with chrysocolla. The author is of opinion that the dioptase described above has been formed from the chrysocolla by the action of water. Very fine botryoïdal malachite occurs associated sometimes with chrysocolla and cuprite, in the same locality in Peru. C. A. B.

On Unghwarite, Nontronite, Gramenite, &c. By A. Kenngott (*Jahrb. f. Min.*, 1878, 180—185).—A. Scrauf (*Jahrb. f. Min.*, 1877, 256) gave the results of two analyses of chloropal from Mugrau, Bohemia, which he found to agree with an analysis of *nontronite* by Berthier; therefore nontronite was a variety of chloropal. Kenngott objects strongly to the name chloropal, as the minerals included in the so-called "chloropal-group" of Dana (including unghwarite, nontronite, pinguite, bole, and gramenite) are not true opals. Schrauf's analyses furnished the following, viz.:—

	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Alkalis.	SiO_2.		H_2O.	
1.	27·50	4·16	2·97	1·77	traces	43·98	(by diff.)	19·62	= 100·00
2.	28·91	3·19	3·35	2·84	—	42·43	(direct)	18·32	= 99·53

If the alumina be considered a vicarious constituent, replacing ferric oxide, and the magnesia a vicarious constituent replacing calcium oxide, and both calculated into the corresponding amounts of ferric oxide and calcium oxide, also if the resulting percentages are then calculated (the percentage of ferric oxide in each analysis being made identical), the composition of the mineral is as follows, viz.:—

	Fe_2O_3.	CaO.	SiO_2.	H_2O.
1.	32·00	5·13	41·44	18·50 = 97·07
2.	32·00	6·93	40·57	17·31 = 96·81

From these calculated percentages it is evident that the relative proportions are nearly $10H_2O$, $1RO$, $2Fe_2O_3$, $7SiO_2$. Schrauf assigned to the mineral the formula $Ca_2Mg_2Al_2Fe_{14}Si_{28}O_{84} + 40H_2O$. The author points out that it would probably have been more correct had Schrauf named the mineral from Mugrau, *nontronite*. If Berthier's analysis of nontronite be treated in the same way as the above, results are obtained which agree closely with them, with the exception of the percentages of the RO metals. These differences are observed in the other allied minerals, whence the author concludes that unghwarite, nontronite, gramenite, pinguite, &c., are only impure varieties of a mineral species which is essentially a hydrated ferric silicate, whose true composition yet requires to be ascertained. C. A. B.

Mineralogical Notices. By S. R. Paijkull (*Jahrb. f. Min.*, 1878, 209—210).—*Eucrasite, a New Mineral from Brevig.*—This mineral is found upon one of the small islands in Brevigsfjord. Crystal system, probably rhombic. Sp. gr. (at 15° C.) = 4·39. H. = 4·5 to 5. Blackish-brown, streak brown, uneven fracture, fuses before the blowpipe on the edges and becomes lighter in colour. Borax bead in the oxidising flame yellow, in the reducing flame violet. Microcosmic salt dissolves it, leaving a skeleton of silica. Partially soluble in hydrochloric acid, with evolution of chlorine; completely soluble in sulphuric acid. Chemical composition as follows, viz.:—

SiO_2.	TiO_2.	SnO_2(?)	ZrO_2.	MnO_2.	ThO_2.	CeO_2.	Ce_2O_3.	$La_2O_3Di_2O_3$.
16·20	1·27	1·15	0·60	2·34	35·96	5·48	6·13	2·42

Y_2O_3.	Er_2O_3.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
4·33	1·62	4·25	1·77	4·00	0·95	0·11	2·48	9·15

Formula corresponding with the above $(\frac{3}{8}RO_2 + \frac{1}{6}R_2O_3 + \frac{1}{4}RO)$ $SiO_2 + 2H_2O$. The author considers it probable that eucrasite is identical with the polycrase (thorite) from Brevig, of Scheerer and Breithaupt, and with the polymignite of Möller.

Picrotephroite from Laangban is a light red mineral, and may be considered to be tephroite in which the manganese has been replaced by magnesium. Its chemical composition is as follows, viz. :—

SiO_2.	MnO.	CaO.	MgO.	Loss on ignition.	
33·70	51·19	0·95	12·17	0·44	= 98·45.

Manganous Serpentine from Laangban.—Colour and streak brown; uneven fracture; brittle. Decrepitates before the blowpipe, and is scarcely fusible even in fine splinters. Dull on broken surfaces; vitreous lustre. Is found pseudomorphous. Chemical composition as follows, viz. :—

SiO_2.	PbO(?).	Fe_2O_3.	FeO.	MnO.	Al_2O_3.	CaO.	MgO.
42·40	0·30	7·51	1·84	7·77	0·90	2·80	24·60

K_2O.	Na_2O.	P_2O_5.	Loss on ignition.	
0·04	0·47	trace.	10·000	= 98·63.

Formula corresponding with the above = $4RO.3SiO_2 + 2H_2O$.

C. A. B.

Homilite. By Descloizeaux and Damour (*Jahrb. f. Min.*, 1878, 204—205).—This mineral (described by Paijkull, *Jahrb. f. Min.*, 1877, 536) is found at Stockö, near Brevig, accompanied by melinophane and erdmannite. Descloizeaux found that the mineral crystallises in the monosymmetrical system, and exhibits a certain similarity to the forms observed on datolite and gadolinite, the crystals being generally developed irregularly. Inclination of clinoaxis to the vertical axis = 90° 39′. The following forms predominate, viz., ∞P, $\frac{1}{2}P\infty$, 0P, $\infty P\infty$, $P\infty$, $-P$. Cleavage not apparent. H. = 4·5 to 5. Sp. gr. = 3·34. Black vitreous lustre; transparent in thin fragments; grey streak. Horizontal dispersion $\nu > \rho$. Some crystals contain a green double-refracting dichromatic kernel, the outer rind or shell being yellowish and refracting light simply. Homilite evolves water on being heated in a closed tube, fuses easily to a black glass, and dissolves in acid with gelatinisation. An analysis by Damour showed it to have the following composition, viz. :—

SiO_2.	BO_3.	FeO.	MnO.	CaO.	Oxides of Ce, La, and Di.	Na_2O.	H_2O.	
33·00	15·21	18·18	0·74	27·00	2·56	1·01	2·30	= 100·00.

C. A. B.

Daubréelite, the New Meteoric Mineral. By J. L. Smith (*Compt. rend.*, **87**, 338—340).—In the resistance of daubréelite to the action of hydrochloric and hydrofluoric acids, the author has found an easy method of separating it from troïlite and other impurities. Daubréelite thus purified presents itself in small, black brilliant scales, of density 5·01. It is not magnetic, and does not fuse before the blowpipe. It gives an intense green colour to borax, and is completely soluble in hot nitric acid. The mean of four analyses gives the following percentage composition: S 42·69, Cr 35·91, Fe 20·10. The mineral is therefore a double sulphide corresponding with chrome iron in which the oxygen has been replaced by sulphur, thus, $FeS.Cr_2S_3$. No terrestrial mineral of this composition is known. The author found daubréelite in several meteorites in which its presence was not previously known, and he believes that this substance, either in a visible condition, or so disseminated as to be discerned only after chemical treatment, will be found to be universally present in meteorites. R. R.

The Mineral Spring of "Tenninger Bad," Somvixer Tobel, Grisons. By R. Meyer (*Deut. Chem. Ges. Ber.*, **11**, 1521—1526).—Temperature of the spring 14·3°. Sp. gr. 1·002522 at 10·5° compared with distilled water at the same temperature. 10,000 parts of water contain—

Na_2O.	K_2O.	$(NH_4)_2O$.	CaO.	SrO.	MgO.	FeO.
0·0847	0·0532	0·0273	8·3688	0·0957	1·1428	0·0016

Al_2O_3 and H_3PO_4.	SO_3.	Cl.	SiO_2.	CO_2.
0·0008	13·4723	0·0049	0·198	1·7182

Organic matter 1·1130, and traces of MnO, Pb, Cu, Zn (?) and HNO_3.

Although the water at present contains mere traces of iron, a thick ferruginous deposit (containing traces of arsenic) is found at the source of the spring. W. C. W.

Presence of Lithium in the Earths and Water of the Solfatara at Puzzuoli. By S. de Luca (*Compt. rend.*, **87**, 174).—The author allowed 10,000 litres of water, which had been used to levigate 250 cwt. of Solfatara earth, to evaporate spontaneously. From the mother-liquors he obtained a considerable quantity of amorphous matter by desiccation. This yielded a hydrochloride, the spectrum of which showed the brilliant lines of lithium distinctly and the sodium lines feebly, showing clearly that the earths of the Solfatara contain traces of lithium in the form of sulphate, which can be extracted by means of rain-water. Hot water is found in abundance at a depth of from 10 to 12 metres below the surface about the old crater of the Solfatara, containing free sulphuric acid and several other substances. The water is formed both by the vapours of the numerous fumaroles, and by the rain percolating through the porous soil and dissolving on its way the soluble matter contained in it. On

treating this water in the manner described above, the same results were obtained, as far as the presence of lithium is concerned, showing that sulphate of lithium is contained in the trachytic earth and in the hot springs of the Solfatera of Puzzuoli. J. M. T.

Organic Chemistry.

Reactions of the Halogen-compounds of Olefines. By Eltekoff (*Deut. Chem. Ges. Ber.*, **11**, 989—991).—Recent experiments by the author have shown that the haloïd compounds of ethylene, when heated with water and lead oxide, yield glycol and aldehyde; whilst propylene chloride and bromide, under the same circumstances, yield propyl glycol, acetone, and propaldehyde. Similarly isobutylene bromide yields isobutyl glycol and the corresponding aldehyde, and trimethylethylene bromide yields isopropylmethyl ketone. From these results the author concludes that the first product of the action in every case is a glycol, which by elimination of water is partially or entirely converted into aldehyde or acetone. J. R.

A New Unsaturated Hexvalent Hydrocarbon, Diallylene, C_6H_8. By L. Henry (*Compt. rend.*, **87**, 171—173).—The action of PCl_5 on monallyl-acetone is energetic and regular at ordinary temperatures, hydrochloric acid being abundantly disengaged. The product is a mixture of allylmethylchloracetol, $C_3H_5.CH_2.CCl_2.CH_3$, and monochlorodiallyl, $C_3H_5.C_3H_4Cl$, resulting from the former by elimination of HCl. The former is a colourless liquid, with a sharp smell and taste, boiling at 150° with partial decomposition. It is insoluble and denser than water. The monochlorodiallyl, which constitutes about $\frac{4}{5}$ths of the product, is a colourless mobile liquid, lighter than and insoluble in water, but soluble in alcohol and ether, and possessing a sharp smell and taste. Its sp. gr. at 18·2° is ·9197, and it boils at 150° without decomposition. The vapour-density found is 4·15, calculated 4·02. This body forms a tetrabromide, ($C_6H_9ClBr_4$), which the author has not as yet solidified. It disengages hydrochloric acid when treated with sulphuric acid, forming probably a sulphate of acetonic alcohol. Heated with potash under pressure at 100° it yields a hydrocarbon of the formula C_6H_8.

The author regards monochlorordiallyl as a mixture of two isomeric bodies:—(1). $C_3H_5.CH_2.CCl{=}CH_2$; and (2). $C_3H_5.CH{=}CCl.CH_3$, resulting from allylic dimethyl chloracetol, $C_3H_5.CH_2.CCl_2.CH_3$, by elimination of HCl.

According to the author the density of diallylene at 18·2° is ·8579; it boils at 70°; its vapour-density as found is 2·79, calculated 2·76. The author has not obtained the dibromide $C_6H_8Br_2$, although the

tetrabromide is easily formed, and by further action of bromine converted into the hexabromide; both are viscous liquids. By the action of ammonic cuprous chloride it yields a yellow precipitate, $C_6H_7Cu + H_2O$, characteristic of acetylene compounds, and with an alcoholic solution of silver nitrate it gives a precipitate corresponding with $C_6H_7Ag + C_2H_5(OH)$; with an aqueous solution it gives $C_6H_7Ag + H_2O$. The author considers it probable that C_6H_8 contains two isomerides corresponding with the formulæ—

(*a.*) $C_3H_5.CH_2.C{\equiv}CH.$
(*b.*) $C_3H_5.C{\equiv}C.CH_3.$

corresponding to the two varieties of monochlorodiallyl above mentioned. J. M. T.

Action of Nitrous Acid on Unsaturated Hydrocarbons. By P. Tönnies (*Deut. Chem. Ges. Ber.*, **11**, 1511—1512).—When a concentrated solution of potassium nitrite is poured into a glacial acetic acid solution of furfurbutylene, the crystalline compound, $C_8H_{10}.N_2O_3$, is obtained, which yields on reduction $C_8H_{10}O(OH).(NH_2)$. This body forms a platinum salt having the formula $[C_8H_{10}O(OH)(NH_2)HCl]_2PtCl_4$.

Phenylbutylene behaves in a similar way, forming $C_{10}H_{12}$, N_2O_3, and $[C_{10}H_{12}(OH)(NH_2)HCl]_2PtCl_4$.

Styrol, tolylbutylene, anethol, and amylene also form crystalline addition products with N_2O_3. W. C. W.

Some Selenocyanates. By J. W. Clarke (*Deut. Chem. Ges. Ber.*, **11**, 1325—1326).—Amongst the platinum thiocyanates the potassium salt is the best known on account of its beauty and the ease with which it may be obtained. It was thought of interest to prepare the corresponding selenocyanate, but some difficulty was experienced in doing so. When alcoholic solutions of potassium selenocyanate and platinic chloride are mixed, a heavy red-brown precipitate is at once formed, which becomes darker and partly dissolves on boiling. Crystals of the new salt separate out from the filtrate, mixed with a reddish selenium salt; these can be purified by recrystallising from alcohol, although they are rather easily decomposed. The crystals are ordinarily small, but can be obtained as hexagonal tables, almost black in reflected light, and dark garnet-red by transmitted light. Sp. gr. = 3·377 at 10° (weighed in benzene). Analysis gives numbers indicating the formula $K_2Pt(CSeN)_6$. The attempt to prepare gold compounds was only partially successful. When an alcoholic solution of potassium selenocyanate is mixed with neutral gold chloride, a red precipitate falls, consisting mostly of pure selenium. On gradual evaporation, the orange-yellow filtrate deposits a crust of small, dark red prisms, which decompose so easily that only a small quantity was obtained, and this not pure. Analysis gave only approximate numbers, but sufficiently near to indicate that the salt was $KAu(CSeN)_2$, considering the impurity (metallic gold) present, for this salt was

prepared by a method precisely analogous to that by which Cleve prepared his thiocyanate. The attempt to prepare a seleniocyanate similar to the potassium chromothiocyanate, $K_6Cr(CSN)_{12}.8H_2O$, of Roeslar was unsuccessful. Aqueous solutions of chrome alum and potassium selenocyanate mixed together gave rise only to a precipitate of selenium. W. S.

Alcohols in Potato Fusel-oil. By L. Rabuteau (*Compt. rend.*, **87**, 501).—The following table shows the nature, boiling-point, and quantities of the products found in 1 litre of potato fusel-oil:—

	Boiling points. Degrees.	Quantities. c. c.
Isopropyl alcohol	85	150
Propyl alcohol	97	30
Ordinary butyl alcohol	109	50
Normal butyl alcohol	106·9	65
Methylpropyl carbinol	120	60
Ordinary amyl alcohol	128—132	275
Products boiling above 132°, and retaining amyl alcohol	—	170
Water	—	125
Aldehyde, ethyl acetate, and ethyl alcohol	—	75

Trimethylcarbinol also appears to be present. R. R.

Etherification of Primary Alcohols. By N. Menschutkin (*Deut. Chem. Ges. Ber.*, **11**, 1507—1511).—The author has repeated his experiments on the etherification of alcohols by acetic acid at 154° (*Ber.*, **11**, 732), and finds that his former results were not quite correct. He now obtains the following numbers for the (I) absolute, (II) relative initial rate, and (III) limit of etherification.

	I.	II.	III.
Methyl alcohol	55·59	—	69·52
Ethyl „	46·95	70·52	66·57
Propyl „	46·92	70·18	66·85
Normal butyl „	46·85	69·61	67·30
Octyl „	46·59	64·40	72·34
Cetyl „	—	—	80·39
Isobutyl „	44·36	66·66	67·38
Allyl „	35·72	60·12	59·41
Benzyl „	38·64	63·98	60·75

From these numbers it is seen that all the primary normal saturated alcohols, except methyl alcohol, have the same absolute initial rate of etherification, but the absolute initial rate of isobutyl alcohol is less than that of the normal alcohols. The relative initial rate decreases with the increase in molecular weight. The rate of etherification of the unsaturated primary alcohols is less than that of the saturated. The limits of etherification increase with the molecular weight of the

alcohol (methyl alcohol forming an exception), but the limits are lower for the unsaturated than for the saturated alcohols.

W. C. W.

Amyl-compounds. By Flawitzky (*Deut. Chem. Ges. Ber.*, **11**, 992).—The author has obtained from ethylamyl oxide an amyl iodide, having the specific rotatory power + 0·07. This iodide yields a pentylene which boils at 20·2°, has the sp. gr. 0·648 at 0°, and is converted by oxidation with chromic acid into acetone, acetic acid, and another acid, probably isobutyric. The corresponding glycol boils at 201°, and yields by oxidation acetone, traces of an aldehyde, and acids, chiefly isobutyric.

Flawitzky finds that diluted sulphuric acid (1 part of H_2SO_4 and 1 part of H_2O) is the best dehydrating agent for the glycols. With it, trimethylethylene and isopropylethylene glycols yield the same products as with phosphorus pentoxide or zinc chloride, but in much larger quantities. J. R.

Oxidation Products of Diethyl Sulphide and Analogous Compounds. By E. O. Beckmann (*J. pr. Chem.* [2], **17**, 439—477).—The author's researches have added the substance *phenylethylsulphide* to the list of sulphides of alcoholic radicles. This body is produced by heating sodium phenylmercaptide with three times its weight of ethyl iodide at 120° in sealed tubes: the new sulphide boils at 204° (barometer = 743·5 mm.), has a sp. gr. of 1·0315 at 10°, and is a strongly refractive liquid with an exceedingly disagreeable odour.

The melting point of *diisobutylsulphoxide*, $(C_4H_9^s)_2SO$, is determined to be 68·5°, and not 41°, as stated by Saytzeff and Grabowsky (*Annalen*, **171**, 255): this substance is but slightly soluble in hot water, while at the ordinary temperature 2 parts of water dissolve 1 part of the sulphoxide.

The author shows that sulphoxides, as also the corresponding sulphides, are generally oxidised to sulphones by the action of potassium permanganate; sulphones have been thus produced from sulphides containing one or two alcoholic radicles derived from primary or secondary isoalcohols. The following new sulphones have been obtained by the author's method:—*Diisoamylsulphone* (the action of nitric acid upon diisoamylsulphoxide, at moderately high temperatures, results in the formation of isoamylsulphonic acid), *diisobutylsulphone*, *isoamylethylsulphone*, *diisopropylsulphone*, *methylethylsulphone*, *phenylethylsulphone*, and *ethenediethylsulphone*. The sulphones are produced by heating an aqueous solution of the corresponding sulphides with a slight excess of potassium permanganate also in aqueous solution. Details of the purification of each sulphone are given in the original paper.

Sulphones are stable bodies which may be distilled without decomposition; they are not reduced by the action of zinc and dilute sulphuric acid or by hydriodic acid; neither are they attacked by phosphorus pentachloride: sulphoxides on the other hand, are reduced by the reagents named, and are readily reconverted into sulphides by the action of phosphorus pentachloride. Former experiments which were

said to result in the production of diethyl- and dimethyl-sulphide from the corresponding sulphones, by reduction, were certainly erroneous: the sulphones employed probably contained traces of sulphoxides.

Sulphides which contain acid radicles are energetically attacked by potassium permanganate, and are therefore not capable of taking up oxygen without molecular decomposition; *benzoylethylsulphide*, for instance, is split up by permanganate into benzoic and ethylsulphonic acids. Saytzeff (*Zeitschr. f. Chem.*, 1868, 642) has shown that these sulphides are also decomposed by the action of nitric acid.

In connection with this behaviour of acid sulphides, the author examined the action of barium dioxide upon thiacetic anhydride dissolved in absolute ether. The action is an energetic one; the products are barium acetate, and acetyl persulphide $(C_2H_3O_2)_2S_2$.

The author's investigations do not determine with certainty whether sulphones do or do not form compounds with nitric acid.

Sulphoxides containing only univalent radicles form somewhat unstable compounds with nitric acid, containing the elements of one molecule of nitric acid combined with one molecule of sulphoxide.

The following are the leading properties of the new sulphones prepared by the author.

Diisoamylsulphone, $(C_5H_{11}{}^{\beta})_2SO_2$, crystallises in groups of long needles, which are unchanged in air, odourless, but possessed of a sweetish yet burning taste. At 31° the sulphone melts to a colourless liquid, which boils at 295° with very slight decomposition. Water, hot or cold, and aqueous solutions of alkalis, scarcely dissolve diisoamylsulphone, but it is largely soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide; also in concentrated nitric, sulphuric, and acetic acids, from which solvents it is reprecipitated by addition of water.

Diisobutylsulphone, $(C_4H_9{}^{\beta})_2SO_2$, is a colourless syrupy liquid resembling glycerin, having a faint pleasant odour; when surrounded with a freezing mixture the sulphone solidifies to a crystalline mass melting at 17°. The sp. gr. of the sulphone at 18° is 1·0056: the liquid boils at 265° without material decomposition. Hot water dissolves but small quantities of the sulphone, although it is soluble in two parts of water at ordinary temperatures: it is readily soluble in ether, and behaves generally towards solvents similarly to diisoamylsulphone.

Isoamylethylsulphone, $\left.\begin{matrix} C_5H_{11}{}^{\beta} \\ C_2H_5 \end{matrix}\right\} SO_2$, is a thick, colourless liquid without smell, which in a freezing mixture solidifies to a crystalline mass: the solid sulphone melts at 13·5°, the liquid has a sp. gr. of 1·0315 at 18°, and boils at 270°. The action of solvents upon this sulphone is similar to their action, already described, upon diisoamyl, and diisobutylsulphone.

Diisopropylsulphone, $(C_3H_7)_2{}^{\beta}SO_2$, forms colourless crystals without odour. It melts at 36°, forming a liquid which often remains for days without solidifying. This sulphone is readily soluble in cold and in hot water, as also in alcohol, ether, benzene, chloroform and carbon bisulphide: concentrated nitric, sulphuric, or acetic acid likewise dissolves the sulphone, which is not reprecipitated by the addition of water.

Methylethylsulphone, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}SO_2$, crystallises in small brilliant needles which melt at 36° (the liquid often remaining for days without solidifying). It is devoid of odour, and very soluble in water and in alcohol. This sulphone is scarcely soluble in cold ether or in carbon bisulphide, but is dissolved in almost all proportions by benzene, chloroform, and acids. Nitric acid very slowly attacks the sulphone, long continued heating in sealed tubes being necessary for the complete decomposition of the substance.

Phenylethylsulphone, $\left.\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\right\}SO_2$, crystallises in thick colourless tables, devoid of odour (m.p. 42°). The solubility of the sulphone is almost the same as that exhibited by diisopropylsulphone; it is however reprecipitated by water from its solution in acids.

Ethylenediethylsulphone, $\left.\begin{matrix}C_2H_4\\(C_2H_5)_2\end{matrix}\right\}SO_2$, is produced by the action of potassium permanganate upon diethyl sulphide *at the ordinary temperature;* it crystallises in short, hard, colourless needles. It melts at 136·5°, and distils unchanged at a higher temperature. This sulphone is soluble in hot alcohol and water; it is scarcely dissolved by ether, benzene, chloroform, or carbon bisulphide, but is readily soluble in concentrated nitric and sulphuric acids, less so in hydrochloric acid, and with yet greater difficulty in acetic acid: it is decomposed by warm solutions of the alkalis. M. M. P. M.

Glucoside of Buckthorn Berries and Rhamnodulcite. By C. Liebermann and O. Hörmann (*Deut. Chem. Ges. Ber.*, **11**, 952—958).—An examination by the authors of the glucoside extracted by alcohol from the berries of buckthorn (*Rhamnus infectorius*) has led to some results differing from those arrived at by previous experimenters. The glucoside was first prepared pure by Gellatly, who called it *xanthorhamnin*, the name adopted by the authors. It is identical with Schutzenberger's α-rhamnegin. The properties of the substance, as described by these chemists, agree with the observations of the authors.

Xanthorhamnin does not ferment with yeast. When boiled with dilute sulphuric acid it readily breaks up into rhamnetin and sugar (rhamnodulcite), the former of which is deposited in tufts of lemon-yellow needles, agreeing in composition with Schutzenberger's formula, $C_{12}H_{10}O_5$.

Rhamnodulcite the authors find to be (contrary to the observations of Gellatly and Schutzenberger) a crystallisable sugar. It is soluble in water and absolute alcohol, and crystallises from the latter in hemihedral tables. The aqueous solution yields holohedral crystals, which melt at 92—93°. Dried in the air, the sugar has the formula $C_6H_{14}O_6$. When heated, it melts, and at 108° gives off 1 mol. of water: the residual $C_6H_{12}O_5$ solidifies on cooling to a brittle glassy mass, the aqueous solution of which again yields crystalline sugar. Rhamnodulcite is very sweet and agreeable in taste. It does not ferment with yeast. Its action on polarised light is dextro-rotatory. It reduces Fehling's solution on warming. Xanthorhamnin yields about 57 per cent. of the sugar. J. R.

Isodulcite. By L. Berend (*Deut. Chem. Ges. Ber.*, **11**, 1353—1355).—Liebermann and Hörmann obtained a beautifully crystallised sugar, by the decomposition of the glucoside of buckthorn berries (*Rhamnus infectorius*) with acids, which was strikingly like the isodulcite prepared by Hlasiwetz and Pfaundler from quercitrin. On account of certain discrepancies, however, in melting point, &c., they termed it rhamnodulcite. On re-examining the isodulcite of quercitrin the author found that the two sugars are identical. The quercitrin employed was prepared according to the method of Zwengler and Dronke, and the isodulcite therefrom according to that of Hlasiwetz and Pfaundler. Melting points (93—94°) and crystalline forms of the isodulcite and rhamnodulcite were found to be the same. Hlasiwetz and Pfaundler found the melting point to be 105°. The specific rotatory power in Soleil-Scheibler's apparatus was $[\alpha]_D = 8{\cdot}04$. The name rhamnodulcite can thus be dispensed with. Liebermann also points out in a footnote that Schützenberger's rhamnegin-sugar is probably only impure isodulcite, in spite of the difference in its properties. W. S.

"Mercurialine" (Methylamine). By E. Schmidt (*Liebig's Annalen*, **193**, 73—86).—E. Reichardt has described (*Jour. f. prakt. Chem.*, 104, 301) a volatile alkaloïd "mercurialine," which he obtained from *Mercurialis annua* and *Mercurialis perennis*, as having the same composition as methylamine, but differing from it in being an oily colourless liquid at the ordinary temperature, and in forming an oxalate and sulphate whose crystallising characters were not in accordance with those given by Wurtz for the corresponding salts of methylamine.

The author has separated a large quantity of the alkaloïd which exists in *Mercurialis annua*, and has compared it with pure methylamine prepared from caffeine. The results prove that the two alkaloïds and their corresponding salts are in every respect identical, and that Reichardt's "mercurialine" is none other than an aqueous solution of methylamine. It was also found that the oxalate and sulphate of methylamine do not behave in the manner stated by Wurtz (*Annalen*, **76**, 324), but that they are readily crystallisable from water; in fact, agreeing with the results obtained by Reichardt with the oxalate and sulphate of "mercurialine."

Trimethylamine in small quantity was also obtained from *Mercurialis annua*, and its presence there, together with a considerable quantity of the primary base induces the supposition that dimethylamine may also be present. In many plants which the author has examined, he has found a small quantity of trimethylamine accompanying ammonium salts, but has met with no species of plants other than those above mentioned, which contain methylamine, although no doubt methylamine is not confined to them. A. J. C.

Trimethylcarbamine. By W. Rudneff (*Deut. Chem. Ges. Ber.*, **11**, 988).—This body was first obtained by Butlerow as a bye-product in the preparation of trimethylacetic acid. According to the author's observations, it boils at 45°. Its hydrochloride, $C_4H_9NH_2.HCl$, crystallises from alcohol in small laminæ. Its platinum salt forms a

yellow crystalline powder. The amine combines with carbon bisulphide to form the compound $CS(NHC_4N_9)(SNH_3C_4H_9)$, from which, by means of mercuric chloride, tertiary butylthiocarbimide, $C(CH_3)_3N.CS$, is obtained. This last boils at 142°, melts at 10·5°, and has an agreeable aromatic odour. J. R.

Sulphuretted Dicyanodiamine. By B. Rathke (*Deut. Chem. Ges. Ber.*, **11**, 962—967).—The author has obtained a body to which he assigns the constitutional formula, $NH_2.CS.NH.C(NH)NH_2$, by the action of thiocarbonyl chloride or phosphorus pentachloride on thiocarbamide. The reaction with phosphorus pentachloride is represented thus: $3CS(NH_2)_2 + PCl_5 = C_2SN_4H_6.HCl + CS(NH_2)_2.HCl + PSCl_3$.

The new product is a base forming transparent monoclinic crystals, which dissolve in water and sparingly in alcohol, and yield a strongly alkaline solution. When heated above 100°, it melts and is completely transformed into the isomeric guanidine thiocyanate.

The *hydrochloride*, $C_2H_6N_4S.HCl$, forms fine transparent rhombic crystals, which dissolve freely in water and alcohol. With platinic chloride it gives an amorphous dark-coloured precipitate. The *oxalate*, $C_2H_6N_4S.C_2H_2O_4 + \frac{1}{2}H_2O$, forms small granular crystals, sparingly soluble in water. Both salts have an acid reaction. J. R.

Butylchloral Hydrocyanide. By A. Pinner and F. Klein (*Deut. Chem. Ges. Ber.*, **11**, 1488—1499).—Butylchloral hydrocyanide prepared by digesting butylchloral hydrate with aqueous hydrocyanic acid at 100° for several days, forms crystalline plates which dissolve readily in alcohol and in ether, sparingly in water and in benzene, but are insoluble in petroleum ether. This substance melts at 101—102°, and boils with decomposition at 230°.

Action of Ammonia.—When ammonia gas is passed into a solution of butylchloral hydrocyanide in absolute alcohol, ammonium chloride, ammonium cyanate and monochlorocrotonamide (m. p. 112°) are formed, $C_4H_5Cl_3(OH)CN + 4NH_3 = C_4H_5ClO.NH_2 + 2NH_4Cl + NH_4CN$.

A good yield of chlorocrotonamide can be obtained by gently heating a mixture of dry butylchloral hydrocyanide and ammonium carbonate in a sulphuric acid bath, until hydrocyanic acid is no longer evolved, and extracting the residue with ether.

No crystalline compound is formed by the action of aniline on the hydrocyanide.

Monochlorocrotonyl carbamide, $CO(NH_2)NH.C_4H_5ClO$, is obtained by heating a mixture of butylchloral hydrocyanide with urea at 105—110°, until all the hydrocyanic acid is evolved, the residue being then treated with alcohol, and the ammonium chloride washed away by water. This carbamide melts with decomposition at 216°.

With acetyl chloride, butylchloral hydrocyanide forms the compound $C_4H_5Cl_3(OC_2H_3O)CN$. It is a yellow oil, boiling with decomposition between 240° and 250°.

When a solution of the hydrocyanide in concentrated sulphuric acid is poured into water, *trichloroxyvaleramide* or *trichlorovalerolactamide*, $C_4H_5Cl_3(OH)CO.NH_2$ (m. p. 119°) crystallises out. It is very soluble

in alcohol and ether, and sparingly soluble in benzene and in water. The hydrochloride is precipitated from the alcoholic solution of the amide by gaseous hydrochloric acid.

The amide prepared from acetyl-butylchloral cyanide melts at 96°, and is probably a physical isomeride of the preceding compound.

A mixture of trichloroxyvaleramide, and trichlor-oxyvalerimido-ether is formed by passing hydrochloric acid into an alcoholic solution of butylchloral hydrocyanide.

Trichlorobutylidenimide, $C_4H_5Cl_3NH$, obtained by heating a mixture of dry ammonium acetate with butylchloral hydrocyanide, and pouring the product into water, is a crystalline body, which melts at 164—165°, and decomposes on exposure to the light, or when heated to 192°. It is sparingly soluble in cold water and in cold benzene, but dissolves readily in alcohol, ether, glacial acetic acid, in hot water and in hot benzene.

Trichloroxyvaleric or *Trichlorvalerolactic acid*, $C_5H_7Cl_3O_3$, described by Pinner and Bischoff, forms the following salts: $C_5H_6NaCl_3O_3 + H_2O$, loses its water of crystallisation at 100°. The ammonium salt forms small granular crystals, and the lead salt is an amorphous precipitate. The acetyl compound, $C_4H_5Cl_3(OC_2H_3O)COOH + H_2O$, which crystallises in white needles (m. p. 84°), is prepared by digesting the acid with acetic anhydride and pouring the product into cold water. It is insoluble in cold water, and is slowly decomposed by boiling with water. The anhydrous compound forms a thick uncrystallisable syrup.

Ethyl trichloroxyvalerate, $C_5H_6Cl_3O_3.C_2H_5$, forms long prismatic crystals, which melt at 40° and boil at 255°. If this ether is dissolved in alcoholic ammonia, and the solution left at rest for several weeks, a white crystalline crust is formed, which consists of a mixture of ammonium chloride and the amide of *monochlorimidoangelic acid*, $C_5H_7ClN_2O$. The amide is soluble in hot benzene, and is reprecipitated by the addition of light petroleum to this solution. It melts at 118° with decomposition. Platinum chloride and silver nitrate produce precipitates in the aqueous solution. The ketone of *monochlorangelactamide* is obtained on evaporating the alcoholic solution of the amide of monochlorimidangelic acid, $C_5H_7ClN_2O + H_2O = C_5H_6ClNO_2 + NH_3$. When this body is heated, it decomposes without melting.

Monochlorangelactic acid, $C_5H_7ClO_3$, prepared by the reduction of trichlor-oxyvalerianic acid (*Ber.*, **7**, 589) forms the following salts: $(C_5H_6ClO_3)_2Zn$, anhydrous crystals, very soluble in water; $(C_5H_6ClO_3)_2Cu$, pale blue powder insoluble in water and in alcohol: $C_5H_9ClO_3.Ag$, deposited from a hot aqueous solution in pearly needles, is decomposed by boiling with excess of silver oxide, forming monochlorocrotonaldehyde or monochlorocrotonic acid.

Ethyl monochlorangelactate, $C_5H_6ClO_3.C_2H_5$, is a heavy oil, boiling with decomposition at 230°, and is slowly decomposed by water. The *isobutyl* ether boils at 235—240°, and is not decomposed by water at the ordinary temperature.

Monochloro-dibrom-oxyvaleric acid, $C_5H_7ClBr_2O_3$, is prepared by adding bromine to a solution of monochlorangelactic acid in glacial

acetic acid. It is soluble in ether, insoluble in benzene, and melts at 169°.

Dichlorangelic acid, $C_5H_6Cl_2O_2$, is formed when the crude product of the action of phosphorus pentachloride on monochlorangelactic acid is poured into water. It is an oily liquid, which does not form addition products with bromine.

Monochlorangelic acid, $C_5H_7ClO_2$, probably $CH_3.CCl{=}CH.CH_2.COOH$.

The ether of this acid is prepared by the action of zinc and hydrochloric acid on the alcoholic solution of dichlorangelic acid. The free acid obtained by saponifying the ether melts at 103°, and is soluble in hot benzene. W. C. W.

Chloralide and its Derivatives. By O. Wallach (*Liebig's Annalen*, **193**, 1—61).—This paper consists of an historical summary of the work of other chemists on chloralide, and contains also a recapitulation of the author's investigations on the subject, of which abstracts have already appeared in this Journal. A. J. C.

The Acids of Wood-vinegar and their connection with the so-called Wood-oils. By C. Krämer and M. Grodzki (*Deut. Chem. Ges. Ber.*, **11**, 1356—1362).—In a previous paper on crude wood-spirit (*ibid.*, **9**, 1920), the authors indicated the possibility that the intermediate bodies corresponding with xylene and cymene could be obtained by condensation of aldehyde and acetone (methyl-ethyl ketone). Experiments in this direction failed.

The first opinion—that only saturated acids took part in the formation of these bodies—was found untenable, and the authors were gradually led to assume that unsaturated acids must also be present in the mother-substances, a supposition confirmed by experiment. Anderson found that salts could be obtained from the acid fractions of wood-vinegar boiling up to above 160°, which certainly contained propionic and butyric acids, and probably valerianic acid; but he did not isolate the pure acids. The authors therefore examined certain liquors from the works of Kahlbaum, in Berlin, which had been obtained in the preparation of sodium acetate or calcium acetate from wood-vinegar, and laid aside as refusing to crystallise further. After the greater part of the sodium acetate had been removed, the mother-liquors yielded an oil on addition of sulphuric acid, from which the following acids were obtained in the pure state and in considerable quantities:—

Saturated: Formic, acetic, propionic, butyric, and valeric acids.

Unsaturated: Crotonic and angelic acids.

The latter, however, has been recognised only by examination of its salts.

Both crotonic and isocrotonic acids were found to be present, and their occurrence is explained by considering them as formed by the splitting off of two hydrogen-atoms from the normal butyric acid, $CH_3.CH_2.CH_2.COOH$, which first furnishes the unstable isocrotonic acid, $CH_2{=}CH.CH_2.COOH$, which becomes converted into the stable crotonic acid, $CH_3.CH{=}CH.COOH$. For this reason the occurrence

of methyl-acrylic acid, $CH_2{=}C(CH_3).COOH$, would be excluded, and indeed not a trace could be detected.

The well-crystallising calcium salt of angelic acid was found to have the composition of the known one, $(C_5H_8O_2)_2Ca + 2H_2O$. The silver salt of the acid was also obtained, and gave sufficiently good numbers for angelic acid. It differs considerably, however, in several respects, both in behaviour and properties, from the two angelic acids known. Thus the two latter are solid, and melt at 45° and 62°, but this, the former, remained fluid. Fittig has observed that by heating, the lower melting acid passes over into the higher melting one, and that there is an intermediate stage at which the acid remains fluid.

The authors, however, did not realise this in their case. Even on heating for a day the acid failed to pass from the liquid to the solid modification. Also on treating with bromine, a remarkable difference is noticed. Whilst angelic acid gives a solid crystalline dibromo-compound with 1 mol. of bromine, the acid obtained by the authors remained liquid. Towards alkali, however, the latter brominated acid behaves exactly like the dibromangelic acid, viz., it loses CO_2 and leaves behind an oil, which to all appearance is identical with crotonyl bromide. Alhough it is possible that the presence of some impurity may occasion the above differences, yet it is quite possible also that the acid in question may be a third angelic acid analogous to isocrotonic acid.

This demonstration of the occurrence of normal acids and the corresponding unsaturated acids in the complex process of the splitting up of the cellulose molecule by dry distillation is interesting in several ways. Whilst in the butyric acid fermentation, only those fatty acids are formed that have even numbers of carbon-atoms (valeric and propionic acids not being produced), in this case the fatty acids with even and those also with odd numbers of carbon-atoms appear, just as in alcoholic fermentation, in which, however, the alcohols corresponding with these higher acids belong, not to the normal, but to the iso-series.

Starting then from the same cellulose molecule on the one hand and the same sugar molecule on the other, three different kinds of decomposition occur:—

I. *By Alcoholic Fermentation.*—Alcohols with even and odd numbers of carbon-atoms arise, *i.e.*, besides ethyl and propyl alcohols, also isobutyl and isoamyl alcohols.

II. *By Butyric Acid Fermentation.*—Besides acetic acid, normal butyric acid and normal caproic acid are formed, *i.e.*, acids with even numbers of carbon-atoms.

III. *By Dry Distillation.*—Acids with even and odd numbers of carbon-atoms: besides acetic acid, propionic, normal butyric, and normal valeric acids were found.

In No. III a method of complete separation by fractional distillation was found wholly impossible, so heterogeneous is the mixture of bodies, and so many boil at about the same temperature. There are the saturated and unsaturated acids, together with bodies taken up from that portion of the distillate known as the "wood-oils," ketones of the fatty and of the oleic series, as well as mixed ketones of both groups, and also condensation-compounds, all probably present together. W. S.

Angelic Acids of Different Origin. By W. v. Miller (*Deut. Chem. Ges. Ber.*, **11**, 1526—1528).—By oxidising fermentation valerianic acid with potassium permanganate, Neubauer (*Annalen*, **106**, 63) obtained carbon dioxide, oxalic, acetic, and butyric acids, and angelic acid (m. p. 69·5—70°), which solidified in the condenser on distilling the product of oxidation with sulphuric acid. A hydroxy-acid is first formed, which on distillation with sulphuric acid loses water and forms angelic acid. This acid can be isolated, if care is taken to avoid adding an excess of sulphuric acid to the oxidation-product, and the mixture is distilled with steam. *Hydroxyvaleric acid* is an oily liquid, which solidifies after remaining *in vacuo* many days over sulphuric acid. It is neither identical with Rohrbeck's α-methyl-β-oxybutyric acid (*ibid.*, **188**, 229), nor with the α-methyl-α-oxybutyric acid of Frankland and Duppa (*ibid.*, **136**, 9), both of which yield α-methylcrotonic acid on dry distillation.

Neubauer's acid differs from α-methylcrotonic acid in melting point and in its barium salt. Neubauer's barium salt contains two molecules of water, and crystallises in the monosymmetrical system, whereas barium methyl-crotonate crystallises with four molecules of water in the asymmetrical system. W. C. W.

Monosulpholactic Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 1561).—The monosulpholactic acids from pyroracemic acid and from α-chloropropionic acid are identical. Schacht's acid (*Annalen*, **129**, 1) from α-chloropropionic acid was impure: hence the apparent difference between the acid from the two sources.

W. C. W.

Synthesis of Pyroracemic Acid. By L. Claisen and J. Shadwell (*Deut. Chem. Ges. Ber.*, **11**, 1563—1568).—The authors have accomplished the synthesis of pyroracemic acid by means of acetyl cyanide, and have thus proved the correctness of Wichelhaus's assumption that this acid is identical with acetyl-formic acid.

When acetyl cyanide prepared by Hübner's process (*Annalen*, **120**, 334) is mixed with the theoretical quantity of hydrochloric acid, sp. gr. 1·20, acetylformamide separates out: $C_2H_3O.CN + H_2O = C_2H_3O.CO.NH_2$. (In this operation an excess of acid is to be avoided, and the mixture must be well cooled.) The formamide is soluble in water, ether, alcohol, chloroform, and in benzene. The alcoholic solution deposits transparent prisms or plates, which melt at 124—125°, and begin to sublime at 100°, forming crystals resembling benzoic acid.

The amide is converted into pyroracemic acid by the action of a slight excess of dilute hydrochloric acid at 100°: $C_2H_3O.CO.NH_2 + HCl + H_2O = C_2H_3O.COOH. + NH_4Cl$. The acid was identified by conversion into uvitic and dibromo-pyroracemic acids, and into pentabromacetone. W. C. W.

Action of Phosphorus Pentasulphide on Organic Acids. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 1352—1353).—*Pyrotartaric acid.*—When a mixture of pyrotartaric acid and phosphorus pentasulphide is distilled in small retorts, an oil is obtained containing

suspended sulphur. It is insoluble in cold water, smells slightly of hydrogen sulphide. On long digestion with hot water it dissolves, and small quantities of hydrogen sulphide escape. The solution on cooling deposits pyrotartaric acid in yellow crystals, to which traces of a sulphurised body adhere; 26 grams of pyrotartaric acid furnished 18·7 grams crude pyrotartaric anhydride.

Pyroracemic acid.—Only a small amount of decomposition, and small yield of sulphurised substance. 80 grams of pyroracemic acid furnished 27 grams of distillate. This could be separated, by fractionating, into acetic acid, pyroracemic acid, and a high-boiling sulphurised body. With the acetic acid and the pyroracemic acid, there is also a small quantity of a sulphurised body. The sulphurised body was a red neutral oil.

Lactic Acid.—This acid decomposes almost completely, on distillation with phosphorus pentasulphide, into gaseous and partially sulphurised products. The fluid distillate is very small, and contains an oily sulphurised body. The latter was dissolved in alcohol and the solution placed in the exsiccator. Besides the alcohol, some volatile sulphur compounds escaped, communicating to the sulphuric acid an intense red coloration. The neutral residue was a red mobile oily body.

W. S.

Action of Zinc-methyl on the Bromides of Monobrominated Acid Radicles of the α-Series. By M. Kaschirsky (*Deut. Chem. Ges. Ber.*, **11**, 984—987).—Zinc-methyl reacts with α-bromopropionic bromide to form a hexyl alcohol boiling at 118—119°, and solidifying below 25°. The chloride derived from this alcohol boils at about 112°, and solidifies at −2°. The iodide boils at about 140°, and solidifies at −3°. The corresponding hexylene distils between 72° and 74°, and forms with bromine a solid compound melting at 169°. By oxidation the alcohol yields acetone and acetic acid. From these facts the author infers that the alcohol is dimethyl-isopropyl carbinol.

The product of the action of zinc-methyl on α-bromisobutyric bromide is pentamethylethol.

Normal α-bromobutyric bromide reacts with zinc-methyl to form a heptyl alcohol boiling at 138—140°, and remaining liquid at −30°. The corresponding chloride boils at 135—138°, and the iodide at 145—147°. The heptylene derived from the alcohol boils at 92—95°, and forms a liquid compound with bromine. By oxidation, the alcohol yields acetone and acetic acid. The author concludes, therefore, that the alcohol is either dimethyl-butyl carbinol or methyl-ethyl-isopropyl carbinol.

J. R.

Conversion of Nitrils into Imides. By A. Pinner and F. Klein (*Deut. Chem. Ges. Ber.*, **11**, 1475—1487).—*Action of Hydrochloric Acid and Alcohol on Hydrocyanic Acid.*—When gaseous hydrochloric acid is passed into a well cooled solution of hydrocyanic acid in absolute alcohol, a series of explosions takes place, ammonium chloride separates out, and the solution contains a mixture of ethyl formate, ethyl chloride, diethyl-glyoxylamide, and ethylic diethyl-glyoxylate.

Ethyldiethylic glyoxylate, $CH(OC_2H_5)_2.COOC_2H_5$, boils at 195—196°,

and is lighter than water. When treated with ammonia, it yields large tabular crystals of *diethyl-glyoxylamide* (m. p. 81—82°) and ethyl alcohol, $C_8H_{16}O_4 + NH_3 = C_6H_{13}NO_3 + C_2H_6O$. If isobutyl alcohol is substituted for ethyl alcohol in the preceding experiment, a mixture of isobutyl chloride, ammonium chloride, and isobutylic di-isobutyl-glyoxylate is formed.

Isobutylic di-isobutyl-glyoxylate, $CH(OC_4H_9)_2.COOC_4H_9$, b. p. 250—252°, is converted into isobutyl alcohol and di-isobutyl glyoxylamide, m. p. 42—45°, by the action of alcoholic ammonia at 100°: $C_{14}H_{28}O_4 + NH_3 = C_{10}H_{21}NO_3 + C_4H_{10}O$. The formation of diethyl-glyoxylic acid and of di-isobutyl-glyoxylic acid from hydrocyanic and hydrochloric acids and alcohol may be represented by the following equations:—

$$2HCN + 2C_2H_6O + 2H_2O = C_6H_{12}O_4 + 2NH_3$$
$$2HCN + 2C_4H_{10}O + 2H_2O = C_{10}H_{20}O_4 + 2NH_3.$$

Neither the imido-ether of formic acid, $HC(NH)OC_2H_5$, nor Gautier's formimido-amide, $CH(NH)NH_2$ (*Compt. rend.*, **65**, 472), were obtained by this reaction.

Action of Hydrochloric Acid and Alcohol on Cyanogen.—When cyanogen gas is passed into a solution of hydrochloric acid in absolute alcohol, in the proportion of 1 molecule of cyanogen to 2 molecules of hydrochloric acid, the chief product is the hydrochloride of oximido-ether, which separates out as a white precipitate, leaving in the mother-liquor a mixture of ammonium chloride, ethyl chloride, ethyl formate, and urethane, which owe their origin to a secondary reaction. The urethane is probably formed by the decomposition of the oximido-ether by hydrochloric acid and water, thus: $C_6H_{12}N_2O_2 + 2H_2O + HCl = C_3H_7NO_2 + CHO_2C_2H_5 + NH_4Cl$.

The *hydrochloride of ox-imido-ether*, $[C(NH)OC_2H_5]_2.2HCl$, is a direct addition-product: $C_2N_2 + 2C_2H_6O + 2HCl = C_6H_{12}N_2O_2.2HCl$. It is insoluble in alcohol and is decomposed by water, forming ethyl oxalate. Aqueous ammonia converts it into oxamide. The free base, obtained by treating the hydrochloride with absolute ether and solid potash, is deposited from an ethereal solution in long thick colourless prisms (m. p. 25°, b. p. 170°). If isobutyl alcohol is substituted for ethyl alcohol, oximido-isobutyl ether and isobutyl urethane are obtained.

Action of Hydrochloric Acid and Alcohol on Propionitril.—The thick oil which is formed when hydrochloric acid gas is passed into a mixture of isobutyl alcohol and propionitril, on decomposition with alcoholic ammonia, yields long prismatic crystals of the *hydrochloride of propionimidamide or propionamidine*, $C_2H_5C(NH)NH_2.HCl$. The hydrochloride is deliquescent, and is very soluble in water and in alcohol, but is insoluble in ether. It melts at 133°, and begins to decompose at 230°. Potash solution converts this substance into an oily liquid, probably propionimidamide, which decomposes slowly in presence of moisture, forming ammonia and propionamide.

By the action of gaseous hydrochloric acid on a well cooled mixture of absolute alcohol and acetonitril, a crystalline compound is formed,

which yields acetimidamide hydrochloride, on treatment with alcoholic ammonia.

β-naphthimido-ethyl-ether hydrochloride, $C_{10}H_7C(NH)OC_2H_5.HCl$, is a crystalline compound, prepared by passing hydrochloric acid gas into a solution of two parts of β-cyanonaphthalene in one of alcohol. It decomposes when heated, forming ethyl chloride and the amide of β-naphthoic acid: $C_{10}H_7C(NH)OC_2H_5.HCl = C_{10}H_7CONH_2 + C_2H_5Cl$. The free imido-ether is obtained by the action of aqueous ammonia on the hydrochloride. It is an oily liquid, insoluble in water, but soluble in alcohol, ether, and benzene.

Alcoholic ammonia converts the hydrochloride into *β-naphthimido-amide hydrochloride*, $C_{10}H_7C(NH)NH_2.HCl$, which crystallises in pearly needles (m. p. 224—226°). The crystals are soluble in water and in alcohol, and turn red on exposure to the light.

By shaking up the hydrochloride with caustic soda, the free base is obtained in the form of an oily liquid, which crystallises in a vacuum.

β-naphthimido-isobutyl-ether hydrochloride, $C_{10}H_7C(NH)OC_4H_9.HCl$, prepared by passing hydrochloric acid gas into a solution of β-cyano-naphthalene in isobutyl alcohol, melts with decomposition at 140°, forming β-naphthamide. *β-naphthimido-isobutyl ether* is deposited from an ethereal solution in long white needles (m. p. 38°), which darken on exposure to the light. On boiling with acetic anhydride, *β-naphthimido-acetate*, $C_{10}H_7C(NH)OC_2H_3O$, is formed. This substance is deposited from a hot alcoholic solution in silky-white needles (m. p. 150—152°). W. C. W.

Action of Iodine on Thiocarbamides. By W. Rudneff (*Deut. Chem. Ges. Ber.*, **11**, 987).—The reaction of diphenylthiocarbamide with iodine results, according to Hofmann, in the formation of phenylthiocarbimide, triphenylguanidine hydriodide, and free sulphur. The author finds, however, that aniline hydriodide is also amongst the products of the reaction, which he represents thus:—
$3CS(NHC_6H_5)_2 + I_2 = 2CSNC_6H_5 + CN_3H_2(C_6H_5)_3.HI + C_6H_5NH_2.HI + S$.

Again, the action of iodine on the ethylamine salt of ethylthiocarbamic acid is represented by Hofmann as follows:—
$CS(NH.C_2H_5)(SNH_3.C_2H_5) + I_2 = CSNC_2H_5 + C_2H_5NH_2.HI + HI + S$.

But, according to the author, this equation expresses only the first phase of the reaction, for the products include also carbon bisulphide and diethylthiocarbamide, which are the results of secondary actions. The reaction in its entirety is represented thus:—
$5CS(NH.C_2H_5)(SNH_3.C_2H_5) + 3I_2 = 2CSNC_2H_5 + 2CS_2 + 6C_2H_5NH_2.HI + CS(NHC_2H_5)_2 + 3S$. J. R.

Dimethyluric Acid. By C. J. Mabery and H. B. Hill (*Deut. Chem. Ges. Ber.*, **11**, 1329—1332).—When dry neutral lead urate is heated with excess of methyl iodide, dimethyluric acid is easily formed, but the lead salt is not completely decomposed, the product being a mixture of the mono- and dimethyl-compounds. A little more than the theoretical quantity of methyl iodide, diluted with an equal weight of ether, should be used. The decomposition proceeds rapidly at 165°,

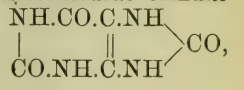
and is completed in 15 to 20 hours. To prevent formation of the mono-compound, potassium urate containing some excess of potassium hydroxide, was used for precipitating the lead salt. The product of the reaction was boiled with water, the dissolved lead removed by sulphuretted hydrogen, and the crystals which separated out on cooling, were recrystallised from hot water. *Dimethyluric acid* forms small oblique prisms containing 1 molecule of water. From saturated solutions it sometimes separates at temperatures near 100° in thick prisms, pointed at both ends and anhydrous. The acid fuses only at a high temperature, with partial decomposition and sublimation. It dissolves in 200 parts of boiling and 800 parts of cold water, scarcely at all in alcohol, ether, and glacial acetic acid. It is easily taken up by concentrated sulphuric and hydrochloric acids, and on dilution again crystallises out. If the acid be dissolved in a little hot potash-solution and alcohol be added, the salt, $K_2C_5(CH_3)_2N_4O_3.4H_2O$, precipitates in silky needles, very soluble in water, and not quite insoluble in alcohol. A similar salt, $Na_2C_5(CH_3)_2N_4O_3.4\frac{1}{2}H_2O$, less soluble in alcohol, is obtained by using soda solution.

$BaC_5(CH_3)_2N_4O_3.3H_2O$, obtained by dissolving the acid in baryta-water, separates out on cooling in flat transparent prisms, soluble with difficulty in cold water, more easily in hot.

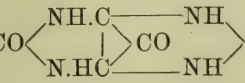
$Ba[C_5H(CH_3)_2N_4O_3]_2\ 3H_2O$ is obtained by boiling an aqueous solution of the acid with barium carbonate, and precipitating with alcohol. The salts, $NaC_5H(CH_3)_2N_4O_3.2H_2O$ and $KC_5H(CH_3)_2N_4O_3.1\frac{1}{2}H_2O$, may be prepared in a similar manner. By these salts the dimethyluric acid is well characterised as a bibasic acid. Heated at 170° with concentrated hydrochloric acid, the acid decomposes into carbon dioxide, ammonia, methylamine, and glycocine, according to the equation:—

$$C_5H_2(CH_3)_2N_4O_3 + 5H_2O = 3CO_2 + NH_3 + 2CH_3NH_2 + C_2H_5NO_2.$$

The evidence thus obtained proves that the two hydrogen-atoms in the uric acid, replaceable by metals, are directly combined with two distinct nitrogen-atoms. If these two hydrogen-atoms be replaced by methyl, then the two remaining hydrogen atoms can be exchanged for metals. This relationship finds a simple explanation only by the assumption that uric acid contains the group NH four times. This requirement is expressed by two only of the various structural formulæ proposed for uric acid, viz., by that of Medicus,



and by that of Fittig,



W. S.

Action of Zinc Chloride on Methyl Alcohol. Hexmethylbenzene. By Le Bel and Greene (*Compt. rend.*, **87**, 260).—The experiment was conducted in the same way as with butyl alcohol (*Bull. Soc. Chim.*, 1878, **29**, 306). The principal products of the action were marsh-gas, a crystalline body, water, methyl ether, and various oils. Traces of methaldehyde, and of propylene, butylene, and other hydrocarbons were also formed. The crystalline body above mentioned amounts to about 0·5 per cent. of the alcohol employed.

After purification from a trace of methaldehyde, oily matters, and a volatile chlorine compound, it forms laminæ melting at 150°, and boiling at 259—260°; it does not combine with bromine. Its analysis leads to the formula $C_{12}H_{16}$, and a comparison of the body and its compound with picric acid with specimens of hexmethylbenzene and its picrate, showed the two to be identical. C. W. W.

On Dinitroparadibromobenzenes and their Derivatives. By P. T. Austen (*Amer. J. Sci.* [3], **16**, 46). Third Paper.*—*β-Dinitroparabromophenol*, $C_6H_2(NO_2)_2BrOH$.—This compound is prepared by treating β-dinitroparadibromobenzene in dilute alcoholic solution with potassium nitrite, and decomposing the resulting potassium salt with hydrochloric acid. It forms, when crystallised from water or alcohol, long, flat, very thin, glittering needles, melting at 71° (78° Körner), and volatilising unchanged when gently heated. Exposed to the air it turns red, probably owing to the presence of ammonia. Heated under water, it melts to a yellow oil. Heated with concentrated sulphuric acid, it evolves nitrous acid, and forms a sulphonic acid (?). On platinum foil, it burns with a luminous, yellow, smoky flame. When thrown on red-hot foil, it deflagrates. Heated with fuming nitric acid, it forms *picric acid*. It is difficultly soluble in boiling water, still less so in boiling dilute hydrochloric and nitric acids; easily soluble in boiling sulphuric acid; very easily in hot alcohol, glacial acetic acid, and aniline; less so in carbon bisulphide.

Silver β-dinitroparabromophenate, $C_6H_2(NO_2)_2BrOAg$.—Splendid glittering red needles, with brilliant green reflex, difficultly soluble in hot water, easily in alcohol. When dry, the salt deflagrates on heating; thrown on a hot surface, it explodes. The *potassium salt* forms long glittering red needles, with greenish reflex, difficultly soluble in boiling water. The *barium salt*, $[C_6H_2(NO_2)_2BrO]_2Ba$, forms saffron-yellow needles, moderately soluble in water and alcohol. Heated in a flask, it explodes, covering the sides with carbon. The *ammonium salt* forms bright-red silky needles, soluble in boiling water and in alcohol. Volatile at 140° to a red sublimate; above that temperature it is decomposed, partially recombining on cooling. The *copper salt* is obtained by treating with glacial acetic acid the product of the action of cupric carbonate on the phenol in alcoholic solution, and diluting with water until the blue colour changes to brown; the salt then separates in short, brown glittering needles, insoluble in water and alcohol, moderately soluble in boiling acetic acid. None of these salts contain water of crystallisation, differing in this respect from the salts of the isomeric dinitrobromophenol obtained by Armstrong (*Ber.*, **6**, 649). The formation of β-dinitroparabromophenol affords a convenient method of separating β-dinitroparadibromobenzene from the α- and γ-compounds, which are unaffected by potassium nitrite.

C. W. W.

Some Addition-products of Trinitrobenzene and other Nitro-compounds. By E. Hepp (*Bull. Soc. Chim.* [2], **30**, 4).—A

* Compare this Journal, 1876, ii, 406 and 513.

solution of trinitrobenzene in benzene deposits large prismatic crystals, which lose their benzene on exposure to the air; they consist of a compound of 1 molecule of each of the constituents, $C_6H_3(NO_2)_3$ and C_6H_6. A similar compound with naphthalene forms long white needles, melting at 152—153°, and losing their naphthalene at the ordinary temperature, or on recrystallisation from alcohol. Anthracene and phenanthrene appear to form similar compounds with trinitrobenzene. The compound with aniline, $C_6H_3(NO_2)_3.C_6H_7N$, crystallises in red needles melting at 123—124°, and is nearly insoluble in cold alcohol; it might be used with advantage for the preparation of pure trinitrobenzene free from dinitrobenzene. The analogous compound with dimethylaniline melts at 106—108°. Both compounds are easily decomposed, either by exposure to the air, by washing with alcohol, or by dilute acids.

By the action of aniline on an isomeric trinitrobenzene (from para-dinitrobenzene, m. p. 171°), red needles melting at 153° were obtained. Analysis led to the formula $C_6H_3(NO_2)_2NHC_6H_5$, which is that of a dinitrodiphenylamine. The alcoholic mother-liquors contained a diazo-amidobenzene, produced by the action of nitrous acid on the excess of aniline.

The addition-products of picramide with aniline obtained by the author differed from those described by Mertens, in that they lost the whole of their base on exposure to the air. Ordinary trinitrotoluene (m. p. 82°) forms compounds exactly similar to those of trinitrobenzene. From this similarity between trinitrobenzene, trinitrotoluene, and picric acid, the author supposes that the NO_2-groups are similarly situated; trinitromesitylene, however, which, according to this hypothesis, should form a compound with aniline, has as yet refused to do so.

No compound of aniline with a dinitro-compound has hitherto been obtained, but compounds of these bodies with hydrocarbons are easily formed. Ortho- and para-dinitrobenzene form crystallisable compounds with naphthalene, the para-compound melting at 110—115°.

C. W. W.

Action of Aniline on Glyoxylic Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 1559—1561).—The yellow crystalline precipitate, which is formed by slowly adding aniline to dilute glyoxylic acid, is an aniline salt of anilglyoxylic acid, $C_{14}H_{11}N_2O_2$. This body was also obtained by Frankland and Duppa, by adding aniline oxalate to calcium glyoxylate. It is decomposed by boiling water into aniline, carbon dioxide, and a brittle substance, which splits up on distillation into water, aniline, and carbanilide.

W. C. W.

Paraxylidine. By W. Schaumann (*Deut. Chem. Ges. Ber.*, **11**, 1537—1538).—Mononitroparaxylene (b. p. 234—237°), prepared from paraxylene (m. p. 15°, b. p. 136°), was reduced by acetic acid and iron filings, and the mixture distilled in a current of steam. Paraxylidine sulphate crystallised out on evaporating the distillate with sulphuric acid. The free base was obtained by adding excess of sodium carbonate to a solution of the sulphate, and distilling in steam.

Paraxylidine is a colourless liquid, which turns yellow on exposure to the air. It boils at 220—221°, and is soluble in hot water. Its salts crystallise well from acid solutions, but their neutral solutions split up on boiling.

Paraxylidine sulphate $[C_6H_3(CH_3)_2NH_2]_2H_2SO_4$, crystallises in colourless plates. The *hydrochloride*, $C_6H_3.(CH_3)_2NH_2.HCl + H_2O$, forms large glistening plates, having a faint pink colour. It is more soluble than the sulphate. At 125—130°, its water of crystallisation is expelled, and the anhydrous salt sublimes.

The *nitrate*, $C_6H_3(CH_3)_2NH_2.HNO_3$, forms pink needle-shaped crystals.

The *oxalate* forms thick prisms, having a pink colour. On heating to 125—130°, it splits up into water and *oxalparaxylidide* $[C_6H_3(CH_3)_2NH]_2C_2O_2$. This body is soluble in alcohol and in ether; it sublimes without melting at 125°, forming slender silky-white needles.

Acetoparaxylidide (m. p. 138—139°) separates out as a crystalline mass on boiling paraxylidine in glacial acetic acid. It is converted into *nitracetoparaxylide*, $C_6H_2(CH_3)_2NO_2NH.C_2H_3O$, by the action of fuming nitric acid. This nitro-compound is a yellow crystalline powder (m.p. 192°). W. C. W.

Oxidation of Sulphamidoxylene. By M. W. Iles and Ira Remsen (*Deut. Chem. Ges. Ber.*, **11**, 1326—1329).—Jacobsen (*ibid.*, **11**, 893) assumed that the authors' sulphaminetoluic acid was not a pure product; but as they have obtained the acid crystallised in beautiful long needles with constant melting point of 254·5—255° (corrected), they consider his supposition to be unfounded. The oxy-acid obtained was also doubtless pure, and crystallised in long lustrous needles, m. p. 174—175°, which is a little higher than Tiemann and Schotten found for their orthohomoparoxybenzoic acid. The two acids are, however, said to be identical. Both contain half a mol. of water of crystallisation, both melt at almost exactly the same temperature, and neither gives any coloration with ferric chloride.

If a mixture of the two sulphamidoxylenes be oxidised with the chromic acid mixture until the oil swimming on the solution has entirely disappeared, a pure sulphaminemetatoluic acid is obtained (m. p. 254·5—255°, corrected). The product was always dissolved in sodium carbonate and the solution evaporated to a small bulk. On cooling some unaltered amide crystallised out. This was filtered off, the filtrate diluted, and the acid precipitated by addition of hydrochloric acid. After twice recrystallising it was pure.

It is not disputed that Jacobsen has obtained an acid by oxidising the amide melting at 95—96°, but the behaviour of this acid with chromic acid mixture must certainly be different from that of the sulphaminetoluic acid. That a mixture of isomeric xylene substitution products can furnish a single compound on oxidation is a fact pretty well settled by other investigators.

(1.) Nitroxylene, obtained by the direct action of nitric acid on xylene, yields a nitrotoluic acid. (Beilstein and Kreüsler.)

This nitrotoluic acid is *not* converted by chromic acid into a bibasic acid.

(2.) Chloroxylene, obtained direct from xylene, yields a chlortoluic acid. (Vollrath.)

(3.) Bromoxylene, obtained direct from xylene, yields a bromtoluic acid. (Fittig, Ahrens, and Mattheides.)

Researches are to be carried out as soon as possible to determine the connection between the nitrotoluic acid (m. p. 203°), the bromotoluic acid (m. p. 205—206°), and the sulphaminemetatoluic acid. It is probable that all these bodies are similarly constituted.

Jacobsen contests the correctness of the conclusion that, because the amide contains a CH_3-group in the ortho-position and a second in the para-position with respect to the sulphamide group, the product necessarily furnishes a stable monobasic acid. However, it is well known that ortho-compounds behave in a peculiar manner towards chromic acid, and some observations show that they are more stable than the isomeric compounds of the other groups.

An error made both by the authors and by Jacobsen is now corrected. The acid formed by oxidation of sulphaminetoluic acid with potassium permanganate is not sulphamineisophthalic acid, but sulphoisophthalic acid. This the authors conclusively prove. W. S.

Oxidation of Metaxylenesulphamide. By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **11**, 1529—1533).—The author denies that the results of his experiments agree with those of Remsen (*Ber.*, **11**, 1328).

W. C. W.

Condensation-products of Tertiary Aromatic Bases. By O. Fischer (*Deut. Chem. Ges. Ber.*, **11**, 950—952).—It has been shown in previous papers that dimethylaniline reacts with benzaldehyde and with furfural to form bodies having the respective formulæ $C_{23}H_{26}N_2$ and $C_{21}H_{24}N_2O$. In the present paper the author describes two new bodies of the same class.

Dimethylaniline reacts with *chloral* in the manner indicated by the equation $Cl_3C.COH + 5C_6H_5N(CH_3)_2 = 3HCl + H_2O + \{C_6H_4N(CH_3)_2\}_3C.CH\{C_6H_4N(CH_3)_2\}$. The product, which must be regarded as a substituted pentaphenylethane, crystallises in colourless needles. It yields by oxidation a blue colouring matter.

A mixture of dimethylaniline and *benzhydrol*, when treated with phosphorus pentoxide, yields *dimethylamidotriphenylmethane* in nearly theoretical amount. This body is a feeble base. It crystallises from alcohol in colourless needles, which melt at 132—133°. J. R.

Cyanoguanidines. By O. Landgrebe (*Deut. Chem. Ges. Ber.*, **11**, 973—978).—In a previous paper the author stated that dicyanodiphenylguanidine reacts with aniline hydrochloride to form a base which he called *β-dicyanotriphenylguanidine*. He has since found that the same base is formed also by the reactions of *α*-dicyanotriphenylguanidine with aniline and toluidine hydrochlorides. The base, unlike the *α*-dicyanoguanidines, is not decomposed by boiling with alcoholic potash or soda, but when heated at 100° for some hours in sealed tubes, it is resolved into aniline, ammonia, oxalic acid, and carbon dioxide.

β-Dicyanoditolylphenylguanidine.—This base is formed by the action of aniline hydrochloride on dicyanoditolylguanidine. It crystallises

from alcohol and water in yellowish needles, having the formula $C_{23}H_{21}N_5 + \frac{1}{2}H_2O$. The base dissolved in alcohol is converted by prolonged boiling with hydrochloric acid into ditolylparabanic acid. It yields an orange-yellow amorphous platinum salt, $2(C_{23}H_{21}N_5,HCl).PtCl_4$.

β-Dicyanotritolylguanidine.—This substance is formed, together with ditolylparabanic acid, on boiling dicyanoditolylguanidine with hydrochloric acid. It crystallises in pale-yellow needles, which melt at 184°. By prolonged boiling with alcohol and excess of hydrochloric acid it yields ditolylparabanic acid. J. R.

Benzaldiacetonamine. By W. Heintz (*Liebig's Annalen*, **193**, 63—72).—By boiling for some time a mixture of acid oxalate of diacetonamine, benzaldehyde and alcohol, the oxalate of benzaldiacetonamine is formed, from which the free base can be obtained by treatment with potash. The base separates as an oily layer, which solidifies on cooling. It dissolves readily in ether, crystallising therefrom in large colourless prisms, and is soluble in alcohol, but with difficulty in water. It melts at 61·2°, and boils at 230°, the distillate consisting of the unaltered substance and another base, which is not yet investigated. Benzaldiacetonamine neutralises acids, forming well-defined salts; its formula is $C_{13}H_{17}NO$.

The *neutral sulphate*, $(C_{13}H_{17}NO)_2H_2SO_4$, crystallises in small needles, which are easily soluble in hot and in cold water, but very difficultly soluble in alcohol, and even more so in absolute alcohol. When it is agitated with ether, a portion of the base is removed and the aqueous solution of the sulphate is rendered acid.

The *nitrate*, $C_{13}H_{17}NO.HNO_3$ (dried at 105°), crystallises from water in short prisms containing water of crystallisation, which they gradually lose on exposure to air.

Neutral oxalate, $(C_{13}H_{17}NO)_2C_2O_4H_2$, is insoluble in alcohol and in ether, and soluble with difficulty in water, from which it crystallises in prisms. It dissolves more readily in water containing free oxalic acid; from this solution it separates in crystals, which are undistinguishable in properties from the neutral oxalate. The hydrochloride, $C_{13}H_{17}NO.HCl$ (dried at 105°), and the platinum salt, $(C_{13}H_{17}NO.HCl)_2.PtCl_4$, have also been prepared. A. J. C.

Phenylthiocarbamic Acid. By B. Rathke (*Deut. Chem. Ges. Ber.*, **11**, 958—962).—The potassium salt of this acid is formed on heating a mixture of aniline and carbon bisulphide with alcoholic potash: $CS_2 + NH_2.C_6H_5 + KHO = C_6H_5.HN.CS.SK + H_2O$.

The same salt is formed, together with diphenylthiocarbamide and potassium thiocarbonate, on heating an alcoholic solution of equal weights of molecule of aniline and potassium xanthate for some hours. The reactions that take place are represented thus:—

1. $C_2H_5O.CS.SK + NH_2.C_6H_5 = C_6H_5.NH.CS.SK + C_2H_5OH$.
2. $C_2H_5O.CS.SK + 2(NH_2.C_6H_5) = (C_6H_5NH)_2CS + C_2H_5OH + KHS$
3. $C_2H_5O.CS.SK + KHS = (SK)_2CS + C_2H_5OH$.

Potassium phenylthiocarbamate, when pure, forms transparent

golden-yellow monoclinic crystals, which melt in their water of crystallisation below 70°. It dissolves in less than its own weight of cold water. The solution becomes turbid when heated, owing to the separation of diphenylthiocarbamide and phenylthiocarbimide. This and all the other reactions of the acid and its salts are explained by the circumstance that the acid readily breaks up, according to the conditions, in one or other of the ways indicated by the two following equations:—

$$C_6H_5.NH.CS.SH = CSN.C_6H_5 + H_2S;$$
$$C_6H_5.HN.CS.SH = NH_2.C_6H_5 + CS_2.$$

The phenylthiocarbimide and aniline thus produced further react to form diphenylthiocarbamide.

Potassium phenylthiocarbamate undergoes decomposition in the air. Its solution, when boiled with cupric sulphate, yields cupric sulphide and phenylthiocarbimide. The aqueous solution dissolves a large quantity of aniline, forming a liquid which, when boiled, gives off hydrogen sulphide and deposits diphenylthiocarbamide.

Free phenylthiocarbamic acid cannot be obtained by acidifying the potassium salt, because it breaks up at once into carbon bisulphide and aniline, as shown above. J. R.

Pentabromoresorcin. By R. Benedikt (*Deut. Chem. Ges. Ber.*, **11**, 1559).—Aniline acts on pentabromoresorcin, forming tribromaniline and tribromoresorcin, $3C_6Br_5HO_2 + 2C_6H_5.NH_2 + 3C_6Br_3H_3O_2 + 2C_6H_2Br_3.NH_2$. Under similar conditions phenol forms tribromophenol.

Tin and hydrochloric acid reduce pentabromoresorcin, first to tribromoresorcin and then to resorcin. Liebermann's tribromoresorquinone is reduced to tetrabromodiresorcin, $(OH)_2HBr_2C_6.C_6Br_2H(OH)_2$, which crystallises in pink needles. It is reduced by sodium amalgam, forming an amorphous body free from bromine; this yields diphenyl on distillation over zinc-dust. W. C. W.

Fluoresceïn-carbonic Acid. By J. Schreder (*Deut. Chem. Ges. Ber.*, **11**, 1340—1344).—Baeyer's beautiful method of forming condensation-products from phthalic acid and phenols, is founded on the property of phthalic acid to form an anhydride, which afterwards enters into reaction with hydroxybenzenes. It was to be assumed at the outset that acids with neighbouring carboxyl-groups would conduct themselves similarly, and in fact this was found the case with oxyphthalic and pyromellitic acid without, in the first case, the oxy-group prejudicing the reaction. It was of interest to see if trimellitic acid, which is a 1 : 2 : 3 derivative (G. Krinos), would behave in a similar manner. Trimellitic acid prepared from colophony, was converted into the anhydride and fused with resorcin at 200°, and in this way a body very similar to fluoresceïn was obtained, differing only by having an extra carboxyl-group in its composition, and hence named fluoresceïn-carbonic acid. The product is a dry red-brown mass of conchoidal fracture, which may be purified by boiling it with water and solution and fractional precipitation from alcohol. When dry it

formed a light-yellow amorphous powder. Analysis showed a carboxylised fluoresceïn, $C_{21}H_{12}O_7$, or $C_6H_3(CO.OH)<\begin{matrix}CO.C_6H_3(OH)\\CO.C_6H_3(OH)\end{matrix}>O$. It is very sparingly soluble in boiling water and glacial acetic acid, but very easily in alcohol, ether, and benzene. The barium and calcium salts were also prepared. The intention was, by boiling it with the carbonates of barium and calcium, to replace only the hydrogen of the carboxyl-group by metal, but it was found that both the hydroxyl hydrogens were replaced.

Barium Salt.—A blood-red solution was obtained by boiling fluoresceïn-carbonic acid with excess of barium carbonate for a long time. This solution could not be crystallised. The concentrated aqueous solution was precipitated with alcohol, and the barium salt obtained in the form of a beautiful orange-red amorphous powder.

Calcium Salt.—Brown-red amorphous powder, prepared like the barium salt. Both salts are very soluble in water, and on evaporation of their solutions are obtained as cantharides-green amorphous masses.

The above-named remarkable behaviour of the two hydroxyl hydrogens caused the author to investigate Baeyer's fluoresceïn in the same direction. Baeyer says fluoresceïn dissolves in lime- and baryta-water with a red colour. The author finds that it further decomposes the carbonates of barium and calcium, furnishing compounds in which both hydroxyl-hydrogens are replaced by metal. Although apparently stronger, fluoresceïn also, although containing no carboxyl-group, furnishes these salt-like compounds much more easily than the new body with the carboxyl-group.

Barium Salt of Fluoresceïn, $C_{20}H_{10}BaO_5 + 9H_2O$, prepared like that of the carboxylised fluoresceïn, is a carmine-red powder, which after recrystallising from water is obtained in beautiful leafy crystals, containing 9 mols. of water.

Calcium Salt, $C_{20}H_{10}CaO_5 + 4H_2O$.—Slender needles. Prepared like the barium salt. Red-brown colour with green reflection.

Acetyl-product, $C_{25}H_{16}O_9$.—*Fluoresceïn-carbonic acid* was heated with acetic anhydride (5 parts) for 2—3 hours with inverted condenser, and the product treated with alcohol and left for about 12 hours. The solution, poured off from the brown oily drops which had separated, was treated with water, which precipitated acetyl-products as bright-yellow flocks. No salt of this product could be prepared, fluoresceïn-carbonic acid being regenerated.

Dibromofluoresceïn-carbonic Acid.—Fluoresceïn-carbonic acid suspended in glacial acetic acid, dissolves on adding the proper quantity of bromine, and the solution soon solidifies to a crystalline paste. The product, recrystallised from glacial acetic acid, forms beautiful brick-red needles, soluble in alkaline fluids to yellow solution.

Tetrabromofluoresceïn-carbonic Acid.—Prepared like the dibromo-product, only using double the quantity of bromine. A dark-reddish solution, showing no inclination to crystallise, was obtained. The bromine-derivative was therefore precipitated with water. It is a dark orange-red amorphous powder, showing colour reactions with alkalis undistinguishable from those with eosin.

Potassium Salt.—Excess of the acid was treated with potash solution, evaporated, and the concentrated solution treated with alcohol, whereby the salt was obtained in small needles with cantharides lustre. It is undistinguishable from eosin-potassium, and dyes like it. The reduction of the fluoresceïn-carbonic acid with sodium-amalgam did not succeed, for a yellow varnish-like mass easily soluble in alcohol was obtained. The solution brought in contact with alkalis at once oxidises and regenerates the original body. This oxidation takes place partially, even on evaporating the solution on the water-bath.

W. S.

Trinitroso- and Trinitro-phloroglucin. By R. Benedikt (*Deut. Chem. Ges. Ber.*, **11**, 1374—1378).—The discovery of dinitroso-resorcin by Fitz, and of dinitroso-orcin by Stenhouse and Groves, made the existence of the corresponding phloroglucin-derivative highly probable. On adding a concentrated well-cooled solution of potassium nitrite to a solution of phloroglucin in dilute acetic acid covered with a layer of ether, the mixture becomes dark-brown, and after some minutes an acid potassium salt begins to separate. On supersaturating the solution with potassium hydroxide, and adding alcohol, the neutral potassium salt is thrown down in beautiful green needles amounting to about 70 per cent. of the theoretical yield. As this *potassium trinitroso-phloroglucin*, $C_6(NO)_3(OK)_3$, cannot be recrystallised without great loss, it must be dissolved in water and precipitated with alcohol, to which some potassium hydroxide has been added. It is easily soluble in water, with difficulty in dilute potash, quite insoluble in weak alcohol. It may be heated to above 130° without decomposition, but explodes at a high temperature. A drop of sulphuric or nitric acid will also occasion violent explosion. A lead salt of trinitroso-phloroglucin is obtained by precipitating a dilute solution of the potassium salt with lead acetate; it falls as a yellow precipitate. When dried it forms a light cinnamon-brown powder, exploding with violence when heated. Nitroso-phloroglucin can be isolated by cautious decomposition of the lead salt mixed with alcohol, by means of sulphuric acid. On filtering and evaporating the alcoholic solution groups of needles are obtained, which are easily soluble in water and alcohol, insoluble in ether.

There is a law recognised already in relation to the number of nitroso-groups in nitroso-derivatives of the phenols, although the number at present known is so small, viz., that each hydroxyl-group appears to render easier the admission of a nitroso-group. Into the hydrocarbons (benzene and naphthalene) NO is introduced only with difficulty and by indirect means.

The monhydric phenols, phenol, thymol, and naphthol, take up one NO-group with ease.

The dihydric phenols, resorcin and orcin, give dinitroso-derivatives.

The trihydric, phloroglucin phenol, yields trinitroso-phloroglucin.

Trinitro-phloroglucin, $C_6(NO_2)_3(OH)_3 + H_2O$.—On adding powdered potassium nitroso-phloroglucin in very small quantities at a time to a mixture of nitric acid and sulphuric acid, oxidation takes place at the ordinary temperature, and finally yellow needles of trinitro-phloroglucin separate out. The mass is then diluted with water, exhausted

with ether, and the product recrystallised from boiling water. The crystalline form is the hexagonal prism modified by combination with the pyramid and prism of the second order, expressed by the formula $\infty P,P, \infty P_2$.

This body loses its crystalline water at 100°. At 130° it begins to sublime; at 158° it melts without decomposition, but explodes on further heating. It is easily soluble in hot water, alcohol, and ether, and is decomposed by sulphuric acid only at a high temperature. Like picric acid, it possesses great tinctorial power for animal matters, but the tint is richer and more beautiful. Trinitro-phloroglucin gives the isopurpuric acid reaction with potassium cyanide. On reduction with hydrogen sulphide or tin and hydrochloric acid, it appears to form the compound analogous to picramic acid. On boiling the tin solution it becomes decolorised, but no triamido-phloroglucin compound could be obtained.

Salts of Trinitro-phloroglucin.—Trinitro-phloroglucin decomposes carbonates readily, and forms with metals three series of salts containing 1, 2, and 3 equivalents of metal. All are explosive.

The potassium salts are formed by saturating 2 molecules of the nitro-compound with 1, 2, or 3 molecules of potassium carbonate. It is necessary to work with a solution as concentrated as possible. The compound $C_6(NO_2)_3(OK)_3$, consists of orange-red shining needles often an inch long, whilst $C_6(NO_2)_3(OK)_2OH$ is of a deep-yellow colour, and not so shining as the preceding. The compound $C_6(NO_2)_3(OK)(OH)_2 + H_2O$ forms long, silky, sulphur-yellow needles, losing water at 100°, and becoming dull.

All three potassium derivatives are sparingly soluble in cold water. The neutral ammonium derivative behaves like the corresponding potassium compound. The barium compound formed by adding baryta-water to an aqueous solution of trinitro-phloroglucin, consists of microscopically small, sulphur-yellow needles, insoluble in cold or boiling water.

Lead acetate gives in an aqueous solution of the acid an amorphous, flocculent precipitate of lead trinitro-phloroglucin. W. S.

Aurin. By R. S. Dale and C. Schorlemmer (*Deut. Chem. Ges. Ber.*, **11**, 1556).—Aurin is formed, together with formic acid, on heating a mixture of oxalic acid and phenolsulphonic acid or barium phenolsulphonate, or by gradually adding oxalic acid to a mixture of sulphuric acid and excess of phenol. Small quantities of carbon monoxide and carbon dioxide are evolved during the process: $3C_6H_6O + C_2H_2O_4 = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O$. W. C. W.

Aurin. By C. Zulkowsky (*Liebig's Annalen*, **194**, 109—144).—The preparation of aurin, and several of the results described in this paper, have already appeared in the *Deut. Chem. Ges. Ber.*, **10** and **11**, and in this Journal in abstract. Aurin contains 70 per cent. of *pseudorosolic acid.* This body separates out as an amorphous resinous mass on treating commercial aurin with sodium bisulphite and diluting the product with water. On adding strong hydrochloric acid to the filtrate from the pseudorosolic acid, and heating the mixture to

80°, a crystalline precipitate is obtained, which gives off sulphur dioxide when heated to 130°. By carefully crystallising the alcoholic solution of this residue, the following substances can be obtained, viz., two homologous rosolic acids, $C_{19}H_{14}O_3$ and $C_{20}H_{16}O_3$; leucorosolic acid, $C_{20}H_{18}O_3$; and a compound having the composition $C_{19}H_{16}O_6$.

Rosolic acid, $C_{20}H_{16}O_3$, dissolves in alcohol, forming a reddish-yellow solution, which changes to carmine on the addition of alkalis. The alcoholic solution deposits crystals containing 1 molecule of water, which belong to the monoclinic or triclinic systems. The crystals appear dark-red by transmitted, and metallic-green by reflected light. They easily lose their water of crystallisation at 100°. On boiling the alcoholic solution of rosolic acid with zinc-dust and acetic acid, *leucorosolic acid*, $C_{20}H_{18}O_3$, is obtained in the form of pale-yellow, anhydrous rhombic crystals.

Rosolic acid, $C_{19}H_{14}O_3$, crystallises in anhydrous, rhombic plates, possessing a garnet-red colour with a bluish lustre. The leuco-product of this acid has the composition $C_{19}H_{16}O_3$.

The compound $C_{19}H_{16}O_6$ is a derivative of the red rosolic acid, $C_{19}H_{14}O_3$. It crystallises in violet, needle-shaped crystals, which dissolve in alcohol, forming a brownish-yellow solution. The alcoholic solution becomes carmine-coloured on the addition of alkalis; when boiled with zinc-dust and acetic acid it yields the leuco-compound $C_{19}H_{16}O_3$, identical with the leuco-derivative of red rosolic acid. The properties of *pseudorosolic acid* have been previously described (*Ber.*, *loc. cit.*). W. C. W.

Rosolic Acids. By H. Caro and C. Graebe (*Deut. Chem. Ges. Ber.*, **11**, 1348—1351).—*Formation of Dioxybenzophenone from Aurin.*—Aurin was heated with water at 220—250°, and a colourless compound was thus obtained which appeared to be identical with the dioxydiphenyl-ketone of Staedel and Gail, and to which the formula $CO(C_6H_4.OH)_2$ is ascribed. The authors have analysed the dioxy-compound, and also its acetyl- and benzoyl-ether, and found numbers which exactly correspond with those for dioxybenzophenone and its ether. Complete agreement of properties was also found to exist between the above-named colourless body and that obtained by Baeyer and Burkhardt by the action of potassium hydrate on phenol-phthalein, and which is also dioxybenzophenone. Besides the convertibility into aurin, the dioxybenzophenone from either diphenylmethane, phthalein, or from aurin exhibits the following colour reactions. If sodium amalgam be added to a dilute cold aqueous solution of the dioxybenzophenone, no coloration occurs, but if the alkaline fluid poured off from the sodium amalgam be heated to boiling, a beautiful red coloration appears, which disappears on cooling, and can be reproduced by again warming. The absorption spectrum of the very dilute red solution shows a strong dark band in the green. On adding hydrochloric acid to the colourless reduction fluid, it becomes orange-yellow, and on boiling, an orange-yellow precipitate separates, which dissolves in soda solution with violet-blue colour, and is decolorised by excess of the alkaline solution. This is in entire agreement with the observations of Baeyer and Burk-

hardt. On heating aurin with water, besides dioxybenzophenone and carbonised decomposition-products, phenol was formed. The reaction is explained in the following equation, and according to the new aurin formula:—

$$(C_6H_4.OH)_2C\begin{cases}C_6H_4\\ |\\ O\end{cases} + H_2O = CO(C_6H_4.OH)_2 + C_6H_5.OH.$$

Synthesis of Aurin from Dioxybenzophenone.—It was thought probable that aurin might be formed from dioxybenzophenone and phenol. This did not succeed directly, but it was successful through the medium of phosphorus trichloride. Dioxybenzophenone was heated for a short time with phosphorus trichloride, the excess evaporated off on the water-bath, and, after cooling, phenol and some concentrated sulphuric acid added. An evolution of hydrochloric acid begins even in the cold, and the mass becomes yellowish-red. By heating on the water-bath or at 140° the reaction is completed after a short time, and on adding water, aurin separates out. Chlorinated bye-products are formed at the same time. The relations manifested by the decomposition and synthesis of aurin to dioxybenzophenone, which, according to the researches of Städel and Beck most probably contains both hydroxyl groups in the para-position, indicate that in aurin both hydroxyl groups, and in rosaniline both amido groups, are also in the para-position. That the third oxygen atom in aurin and the imido group in rosaniline most likely take the ortho-position, the formation of rosaniline from orthotoluidine, and a rosolic acid from salicylic aldehyde testify. The latter compound, according to the results of Liebermann and Schwarz, is probably identical with aurin. The violet body formed from iodo-dimethaniline (Weber) is against this theory, however, as here one must assume that all three nitrogen atoms are in the same position.

Formation of a Colouring Matter from Monoxybenzophenone and Phenol.—The oxybenzophenone of Döbner and Stackmann was heated with phosphorus trichloride, and then with phenol and sulphuric acid. On treatment with water, a resin separated out, which in appearance resembles crude corallin. This resin contains a colouring matter, and its properties place it in the group of the rosolic acids. By solution in soda and precipitation with sulphurous acid, it is purified, and then forms an orange-red powder which fuses under water to a red-brown resin with green lustre. It dissolves in alkalis with a less intense violet-red than phenol-phthalein. The solutions gradually decolorise. With alkaline hydrogen sulphites it forms colourless solutions, and it combines with hydrocyanic acid like rosolic acid. The authors believe from these observations that this compound is a rosolic acid, $(C_6H_5)(C_6H_4.OH)C\begin{cases}C_6H_4\\ |\\ O\end{cases}$. It is considered very probable that Döbner and Stackmann had this substance in their hands when they acted with phenol upon benzotrichloride, and that it was actually contained in the red-brown resin which they describe in their paper as the product of the reaction. On repeating their experiments the

authors obtained a colouring matter on treatment with hydrogen sodium sulphite, the properties of which agree with those of the compound from oxybenzophenone. W. S.

Reduction of Acetophenone. By K. Buchka (*Deut. Chem. Ges. Ber.*, **11**, 1550—1551).—By the action of sodium amalgam on acetophenone, Emmerling and Engler obtained a pinacone boiling at 202°, and a secondary ethyl benzene alcohol, whilst the author by the same reaction obtained only pinacone. The author considers that the low boiling point of the pinacone is probably due to its splitting up into equal molecules of acetophenone and the secondary alcohol.

W. C. W.

A Sulphuretted Derivative of Acetophenone. By C. Engler (*Deut. Chem. Ges. Ber.*, **11**, 930).—Acetophenone reacts with ammonium sulphide and hydrogen sulphide in alcoholic solution to form a body which the author regards as *thiacetophenone* or a polymeride of it. This substance crystallises from alcohol in colourless or yellowish laminæ, which are insoluble in water, but soluble in ether, chloroform, and benzene. It melts at 119·5°, and sublimes in feathery crystals exhibiting a bluish iridescence. J. R.

Sulphuretted Derivatives of Benzophenone. By C. Engler (*Deut. Chem. Ges. Ber.*, **11**, 922—926).—1. When alcoholic solutions of benzophenone and ammonium sulphide are mixed together and saturated with hydrogen sulphide, the following reactions take place slowly: $C_6H_5.CO.C_6H_5 + H_2S = C_6H_5.CS.C_6H_5 + H_2O$; and $2(C_6H_5.CS.C_6H_5) + H_2S = (C_6H_5)_2CH.S_2.CH(C_6H_5)_2 + S$.

The product is a solid substance crystallising from alcohol in snow-white needles, which melt at 151°. It is identical with the body which A. Behr (*Ber.*, v, 970) obtained by the action of alcoholic potassium sulphydrate on benzophenone chloride.

2. The mother-liquors of the above substance, as prepared by Behr's reaction, yield by further treatment another body which crystallises in small white needles (m. p. 146·5°), and has the composition of *thiobenzophenone*, $C_6H_5.CS.C_6H_5$.

Both these compounds, when cautiously oxidised with chromic acid, yield benzophenone and no intermediate product.

3. Benzhydrol reacts with phosphorus pentasulphide to form the crystalline compound melting at 151° described above, and an oily body, which by treatment with mercuric oxide or chloride yields the compound $[(C_6H_5)_2CH.S]_2Hg$. J. R.

Dibromo-metaxylene-sulphonic Acid. By O. Jacobsen and E. Weinberg (*Deut. Chem. Ges. Ber.*, **11**, 1534—1536).—*Dibromo-metaxylene-sulphonic acid*, $C_6HBr_2(CH_3)_2SO_3H$, separates out in small anhydrous scales when water is added to a solution of dibromo-metaxylene (m. p. 72°) in fuming sulphuric acid. The crystals melt at 165°, and are soluble in hot, sparingly soluble in cold water. The *barium salt* $[C_6HBr_2(CH_3)_2SO_3]_2Ba$, is sparingly soluble in water. $C_6HBr_2(CH_3)_2SO_3Na + 2H_2O$ forms colourless pearly scales, soluble in

hot, and almost insoluble in cold water. The acid chloride, $C_6HBr_2(CH_3)_2SO_2Cl$, crystallises in colourless rhombic plates, which melt at 107°. The amide, $C_6HBr_2(CH_3)_2SO_2NH_2$, forms woolly needles, insoluble in absolute alcohol; they melt at 220°, and begin to decompose at 230°.

A mixture of β-metaxylene-sulphamide (m. p. 96°) and monobromo-β-metaxylene-sulphamide (m. p. 161°) is formed by treating the product of the action of sodium-amalgam on sodium dibromo-metaxylene-sulphonate with phosphorus pentachloride and ammonia. The monobromo-metaxylene-sulphamide crystallises from dilute alcohol or from hot water in long flexible needles. The relation between dibromo-metaxylene-sulphonic acid and the allied xylene derivatives is shown by the following formulæ:—

β-Metaxylene-sulphonic acid.	Monobromo-β-xylene-sulphonic acid.
$C_6H_3(CH_3)(SO_3H)(CH_3)(1:2:3)$.	$C_6H_2(CH_3)(SO_3H)(CH_3)Br(1:2:3:6)$.
M.p. of amide.. 96°.	161°.

Dibromo-β-metaxylene-sulphonic acid.
$C_6H(CH_3)(SO_3H)(CH_3)(Br_2(1:2:3:4:6)$.
M.p. of amide .. 220°.

α-Metaxylene-sulphonic acid.	Monobromo-α-xylene-sulphonic acid.
$C_6H_3(CH_3)(SO_3H)CH_3.(1:3:4)$.	$C_6H_2(CH_3)(SO_3H)(CH_3)Br.(1:3:4:6)$.
M.p. of amide .. 137°.	194°.

W. C. W.

Oxidation of Ditolylparabanic Acid. By O. Landgrebe (*Deut. Chem. Ges. Ber.*, **11**, 978).—By the oxidation of ditolylparabanic acid, $N_2(CO)(C_2O_2)(C_6H_4.CH_3)_2$, with potassium permanganate, the author has obtained an acid agreeing in composition with the formula $N_2(CO)(C_2O_2)(C_6H_4.COOH)_2$. The potassium salt of this acid dissolves easily in water, sparingly in alcohol, and gives crystalline precipitates with salts of the alkaline earths and heavy metals.

J. R.

Parachlorobenzyl Chloride and Bromide. By C. L. Jackson and A. W. Field (*Deut. Chem. Ges. Ber.*, **11**, 904).—The substance described as parachlorobenzyl chloride has hitherto been prepared from the chlorotoluene obtained by the direct action of chlorine on toluene in the cold. But this last product has been shown by Hübner and Majert (*Ber.*, **6**, 790) to be a mixture of ortho- and parachlorotoluene. The authors have therefore prepared parachlorobenzyl chloride from pure parachlorotoluene, and find that it is not a liquid, as was formerly thought, but a solid substance. It crystallises in white brilliant needles or prisms, having a pleasant aromatic odour. It melts at 29°, and volatilises at common temperatures. The vapour acts violently on the mucous membranes. Ether, benzene, carbon bisulphide, acetic acid, and warm alcohol dissolve it easily. It is insoluble in water, and when boiled therewith, it is resolved into parachlorobenzyl alcohol and hydrogen chloride.

Parachlorobenzyl bromide, $C_6H_4Cl.CH_2Br$, similarly prepared, melts at 48·5°, and resembles the chloride in properties. J. R.

Vapour-density of Indigo. By E. v. Sommaruga (*Deut. Chem. Ges. Ber.*, **11**, 1355—1356).—After his investigation on the action of ammonia on isatin, whereby he was led to the conclusion that this body possessed the formula $C_{16}H_{10}N_2O_4$, the author determined the vapour-density of indigo by Habermann's modification of Dumas' method. As a mean of nine determinations he obtained the number 9·45, whilst the formula $C_{16}H_{10}N_2O_2$ requires 9·06. Isatin is totally decomposed before it can be vaporised. W. S.

Action of Ammonia on Isatin. (II.) By E. v. Sommaruga (*Liebig's Annalen*, **194**, 85—108).—The author has proved quantitatively that the action of ammonia on isatin under pressure may be represented by the following equations:—

1. $C_{16}H_{10}N_2O_4 + 2NH_3 = 2H_2O + C_{16}H_{12}N_4O_2$.
 Isatin. Isatin-diamide.

2. $4C_{16}H_{10}N_2O_4 + 7NH_3 = 7H_2O + C_{16}H_{14}N_6O_3 + 3C_{16}H_{11}N_3O_2$.
 Isatin. Oxydiimido-diamido-isatin. Desoxyimido-isatin.

Derivatives of Diamido-isatin.—In addition to the salts, which have been previously described (*Annalen*, **190**, 367—384), the author obtained the chromate, $C_{16}H_{12}N_4O_2.H_2CrO_4$, as an orange-coloured powder, by boiling a solution of the sulphate with potassium dichromate. By the action of sodium-amalgam on diamido-isatin, the sodium salt of dihydro-isatinamide is obtained in long colourless crystals, which are sparingly soluble in cold water: $C_{16}H_{12}N_4O_2 + H_2O + H_2 = NH_3 + C_{16}H_{13}N_3O_3$. The potassium salt resembles that of sodium. The free base is deposited from an alcoholic solution in colourless needles (m. p. 213°), which are sparingly soluble in ether and in water. Diamido-isatin is not acted on by zinc and sulphuric acid, and is with difficulty reduced by tin and hydrochloric acid.

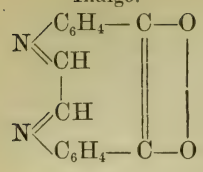
Oxydiimido-diamido-isatin, $C_{16}H_{14}N_6O_3$.—The sulphate and nitrate of this base are crystalline salts. Their solutions are fluorescent. The nitroso-compound has not yet been obtained in a state of purity.

Diamido-hydrindic acid, $C_{16}H_{10}N_2(OH)_2(NH_2)_2$, is obtained in granular crystals by boiling the base with sodium-amalgam and neutralising the product with sulphuric acid. This acid melts at 215—217°, with partial decomposition. It is oxidised by a mixture of sulphuric acid and potassium dichromate, forming *diimido-hydrindin-carbonic acid*, $C_{16}H_{12}N_4O_4$, which crystallises from hot water in colourless glistening needles.

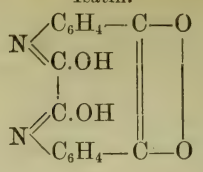
Deoxyimido-isatin is not reduced by sodium amalgam, but is converted into the sodium salt of *oxyamido-hydroisatin*. The same change takes place on boiling amido-isatin with alkalis, $C_{16}H_{11}N_3O_2 + H_2O = C_{16}H_{13}N_3O_3$. On adding sulphuric acid to the sodium salt, oxyamido-hydro-isatin separates out as a yellow flocculent precipitate, which is soluble in hot water, in alkalis, and in acids.

According to the author, the existence of the above compounds shows that the molecules of isatin and of indigo contain 16 atoms of carbon. The following formulæ are proposed for these bodies and their derivatives:—

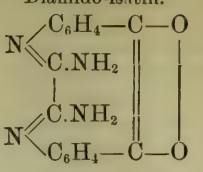
Indigo.



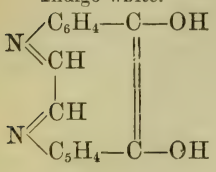
Isatin.



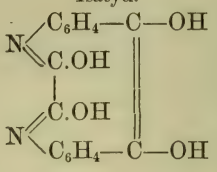
Diamido-isatin.



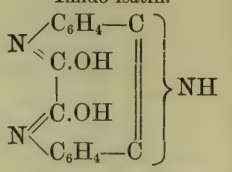
Indigo-white.



Isatyd.



Imido-isatin.



W. C. W.

On Diphenol. By L. Barth and J. Schreder (*Deut. Chem. Ges. Ber.*, **11**, 1332—1339).—By the action of fused potash on phenol, salicylic acid, oxybenzoic acid, and diphenol, $C_{12}H_{10}O_2$, are formed. The latter body began to crystallise after standing for some weeks, and was distilled in a vacuum : the greater portion passed over under a pressure of about 150 mm. between 310—330°, and became a hard crystalline mass, in which two different crystalline forms were easily perceptible, viz., long thin needles and scales. This was dissolved in a large quantity of boiling water, and the very dilute solution (which did not become turbid on cooling) was partly precipitated with lead acetate, the dark brown flocks removed, and the filtrate completely precipitated with lead acetate ; and the bulky white precipitate decomposed with hydrogen sulphide. The solution exhausted with ether yielded, after evaporation, an oil which solidified. This was carefully crystallised from boiling water. The crystals obtained were most clearly of two different forms. No method of separation by means of solvents or precipitants, could be discovered, but by fractional crystallisation from water, a separation could be effected, although with much trouble. The body crystallising in needles was thus obtained in some considerable quantity ; but only enough of the scaly body to enable the authors to study its chemical characteristics. The bulk remained behind, a mixture defying further separation. The needle-shaped body was found to be the most soluble in water, but crystallised out first owing to its preponderating quantity.

The less soluble substance crystallises in small glittering scales. Both have the same formula, $C_{12}H_{10}O_2$, and are isomeric diphenols. The needle-shaped compound was designated *α-diphenol*, the other *β-diphenol*.

α-Diphenol, $C_{12}H_{10}O_2$.—Soluble in water, and easily so in alcohol, ether. chloroform, benzene, &c. Its aqueous solution gives with ferric chloride a pure cornflower-blue coloration, remaining unaltered for a week. Addition of sodium carbonate destroys the colour, and on heating, a red-brown precipitate separates, which however does not consist of ferric oxide. In water the diphenol melts below 100° ; heated alone it melts at 123°. It crystallises anhydrous, and the

vapour-density by Victor Meyer's method was found to be 6·40; calculated 6·44. By distillation with zinc-dust it gave a very rich yield of diphenyl (over 70 per cent.). Heated for some hours at 130°, with potash and methyl iodide and some methyl alcohol in sealed tubes, it yielded dianisoïl.

α-Diphenol-sulphonic acid, $C_{12}H_8(HSO_3)_2O_2$. α-Diphenol warmed with sulphuric acid in a platinum dish until the vapours of the acid began to be given off, and the mass became reddish-brown, solidified on cooling to a granular crystalline mass. It dissolved very easily in cold water. Treatment with lead or barium carbonates in the ordinary way to remove excess of sulphuric acid is inadmissible, since the sulpho-acid itself forms almost insoluble salts with these metals. It is best to add approximately calculated quantities of lead carbonate, and after separating the traces of dissolved lead by hydrogen sulphide, to concentrate to a syrupy consistence. In the exsiccator the syrupy solution solidifies to a light grey crystalline mass. The acid is extremely soluble in water. At 110° it is decomposed, turning brown, and becoming a varnish like and very hygroscopic mass. This decomposition takes place in the air at 100° after long drying. Analysis showed that the body was a disulpho-acid, $C_{12}H_8(HSO_3)_2O_2$.

The sodium salt, $C_{12}H_8Na_2S_2O_8 + 2H_2O$, obtained by exactly saturating the sulphoacid with sodium carbonate, separates in fine stellate groups of needles. The water of crystallisation is driven off at 200°.

Sodium determinations made on crystals obtained by further concentration of the mother-liquor gave a smaller amount of sodium. This observation was made in the case of the other salts, and indicates that a portion of the sulpho-group becomes split up on concentrating the aqueous solution. The potassium salt crystallises likewise in needles with one molecule of water. The barium salt is obtained as a crystalline precipitate, by decomposing the potassium or sodium salt with barium chloride. The crystallisation-water could not be exactly estimated.

Dipyrocatechin, $C_{12}H_{10}O_4$.—If the potassium salt of the disulpho-acid be heated with excess of potash, the fused mass gradually becomes yellow, and on acidifying liberates sulphurous oxide freely. The ether extract obtained in the usual way yields a brownish crystalline mass, consisting of fine interlaced needles, which easily decompose in contact with the air. It was only by sublimation in a stream of hydrogen, that a small quantity was obtained as a colourless crystalline sublimate; the greater portion was, however, decomposed, remaining behind as a blackish-brown syrup. The melting point of the sublimate was 84°. Its aqueous solution gave a bright green colour reaction with ferric chloride, which on addition of very little dilute sodium carbonate solution becomes dark blue, on further addition violet, and finally red. This reaction is the same as that of pyrocatechin, only the first green coloration is brighter. The name dipyrocatechin was chosen in order to recall its formula and the analogous colour reactions.

The colour of the unsublimed product which was analysed, was the same (with ferric chloride and sodium carbonate), only the

green had a shade of brown in it. The reaction is so delicate, that mere traces can be detected. The blue and violet shades are especially intense.

β-Diphenol, when pure, forms small glittering scales. In water it is rather sparingly soluble, and does not fuse therein sooner than the α-diphenol. The aqueous solution gives a bright green colour with ferric chloride. After some time the clear solution becomes turbid, and green flocks separate, leaving the solution colourless. With other solvents it behaves just like the α-diphenol. On distilling with zinc-dust, diphenyl is obtained abundantly. It melts at 190°, is anhydrous, and its vapour-density (Victor Meyer's method) was found to be 6·39 for 6·44 (calculated). Just as with α-diphenol, a dianisoïl was obtained from the β-diphenol. This dianisoïl solidified in a short time after distillation, forming a crystalline mass. Under the microscope octahedra were readily distinguished. The boiling point could not be estimated as the quantity was too small. The authors have proved qualitatively that a number of interesting derivatives may be obtained from both the diphenols, if only a good method of separating these isomerides could be discovered.

Diphenylbenzene.—The residue left on distilling the crude diphenol under diminished pressure was distilled at a higher temperature. A dark yellow mass resembling rosin was obtained, whilst some carbon remained in the retort. The distillate was repeatedly boiled up with water, whereby some α- and β-diphenol were separated. The exhausted residue of dark brown colour was mixed with zinc-dust and distilled in a stream of hydrogen, to ascertain if it still contained diphenol or perhaps a higher condensed product. The product was a yellowish-brown semi-solid mass smelling of diphenyl, and yielding diphenyl as a sublimate on warming on the water-bath and passing a stream of hydrogen over it: the dark residue, when distilled, furnished a yellowish oil which crystallised on cooling. This body was almost entirely soluble in boiling alcohol, which deposited it on cooling in white crystalline flocks (m. p. = 206°). Vapour density (Victor Meyer) = 7·70; calculated for $C_{18}H_{14}$ = 7·94. Thus the body is a diphenylbenzene, and judging from its melting point, is the so-called paradiphenylbenzene, obtained by G. Schulz as a bye-product in the preparation of diphenyl from benzene.

Now although it is possible that this diphenylbenzene is a secondary product arising from the diphenyl, yet regarding the properties of the mother-substance, it seems probable that it is rather formed by reduction from a more highly condensed phenol, triphenol for example.

Of the numerous possible isomerides of diphenol four are known: (1.) That obtained by Griess from tetrazodiphenyl, later by Lincke from phenylparasulphonic acid. (2.) That obtained by Engelhardt and Latschinoff from diphenyldisulphonic acid, and afterwards more closely investigated by Döbner, and (3) and (4), those described by the authors. These bodies are sharply distinguished by their melting points (1), melts at 156—158°; (2) 269—270°; (3) 123°, and (4) at 190°. Heating with zinc-dust does not decompose No. 1, whilst Nos. 2, 3, and 4 yield diphenyl almost quantitatively. The colorations with ferric

chloride and the lead acetate reactions are not stated in the case of the first-named.

As regards constitution, the diphenol of Griess and Linke may best be named paradiphenol. As regards that investigated by Döbner (2), both hydroxyls are contained in one benzene-group, and so the name diphenol does not seem suitable, in so far as it would express that two phenol molecules have united, with loss of H_2, to form one molecule. α- and β-diphenol might perhaps be designated *ortho-* and *meta-diphenol*, in so far as, in their preparation, salicylic acid is formed in predominating proportion, and oxybenzoic acid in smaller quantity, whilst paraoxybenzoic acid is never observed. It is by no means impossible that an ortho-meta-diphenol is likewise produced. It is not to be denied that the mechanism of the reactions in all three cases is very similar, since by fusing phenol with potash the removal of hydrogen at the ortho- and meta-position is effected, and by fusing the phenolparasulphonic acid, the removal of HSO_3 at the para-position; and in all cases the two phenol residues unite to form diphenols.

W. S.

Action of Potash on Tetranitrodiphenyl-carbamide. By S. M. Losanitch (*Deut. Chem. Ges. Ber.*, **11**, 1539—1542).—When a solution of diphenylguanidine or carbanilide in cold concentrated nitric acid, is heated until red fumes are no longer evolved, and the liquid is allowed to cool, tetranitrodiphenylcarbamide is deposited in pale yellow needle-shaped crystals, which are blue or green by reflected light. On boiling tetranitrodiphenylcarbamide with alcoholic potash, it is slowly converted into tetranitrodiphenyl-potassium-carbamide, $CO.[NKC_6H_3(NO_2)_2]_2$, a glistening green crystalline powder, which explodes on heating. This compound is converted into dinitraniline by boiling with water. $CO[NKC_6H_3(NO_2)_2]_2 + 2H_2O = 2C_6H_3(NO_2)_2.NH_2 + K_2CO_3$. Acids convert the potassium compound into tetranitrodiphenylcarbamide, small quantities of dinitraniline and carbon dioxide being also formed. $CO[NKC_6H_3(NO_2)_2]_2 + H_2SO_4 = CO[NH.C_6H_3.(NO_2)_2]_2 + K_2SO_4$.

Tetranitrodiphenylcarbamide forms a yellow crystalline compound with calcium, and a red unstable compound with ammonium.

W. C. W.

Naphthyl-phosphorus and Napthyl-arsenic Compounds. By W. Kelbe (*Deut. Chem. Ges. Ber.*, **11**, 1499—1503).—To prepare *naphthyl-phosphorous acid*, $C_{10}H_7.POH(OH)$, a mixture of mercury dinaphthyl and excess of phosphorous chloride is heated in sealed tubes at 200° for five days; the phosphorous chloride is distilled off; and the residual oily liquid, consisting of impure naphthylphosphorous chloride, is poured into water: $PCl_2C_{10}H_7 + 2H_2O = 2HCl + C_{10}H_7.POH(OH)$. The liquid is boiled to expel the hydrochloric acid, and is mixed with a slight excess of sodium carbonate. The solution is now filtered, and the acid precipitated by the addition of hydrochloric acid. The precipitate is washed with cold and recrystallised from hot water. During this operation, oily drops of *dinaphthylphosphinic acid* remain undissolved. Naphthylphosphorous acid crystallises in small white needles, which are soluble in alcohol and in hot water, but are insoluble in hydrochloric acid, and only sparingly

soluble in ether and in cold water. The dry acid melts at 125—126°, but when boiled in water, it melts before dissolving. Silver nitrate is reduced by this acid.

Diethylnaphthylphosphine, $C_{10}H_7.P(C_2H_5)_2$, is prepared by the action of crude naphthylphosphorous chloride diluted with benzene on a well cooled mixture of zinc-ethyl and benzene. $PCl_2C_{10}H_7 + Zn(C_2H_5)_2 = ZnCl_2 + C_{10}H_7.P(C_2H_5)_2$. The benzene is distilled off from the crude product, and the residue dissolved in hydrochloric acid. Soda is added to the solution, and the phosphine is extracted from the precipitate with ether. It is a yellow oily liquid, boiling with partial decomposition above 360°, and possessing a most repulsive odour. Diethylnaphthylphosphine absorbs hydrochloric acid gas, forming first a solid, and then a liquid compound.

Triethylnaphthylphosphonium iodide, $C_{10}H_7.P(C_2H_5)_3I$, formed by the direct addition of ethyl iodide to diethylnaphthylphosphine, crystallises from an aqueous solution in colourless plates (m. p. 209°).

Dinaphthylphosphinic acid, $PO(OH)(C_{10}H_7)_2$.—The formation of this acid has been already mentioned. The oily drops solidify, forming a white crystalline mass, m. p. 202—204°, soluble in alcohol.

Naphthylarsinic acid, $C_{10}H_2AsO(OH)_2$.—Mercury-dinaphthyl is readily acted on by arsenious chloride, thus, $2AsCl_3 + Hg(C_{10}H_7)_2 = HgCl_2 + 2C_{10}H_2AsCl_2$. The compound is separated from the mercuric chloride by extraction with benzene. The oily liquid left after distilling off the benzene unites with a molecule of chlorine to form $C_{10}H_7AsCl_4$, which is decomposed by water into hydrochloric and naphthylarsinic acids: $C_{10}H_7AsCl_4 + 3H_2O = 4HCl + C_{10}H_7AsO.(OH)_2$. The acid forms needle-shaped crystals (m. p. 197°). Analogous antimony compounds have not been obtained. W. C. W.

Metabenzdioxyanthraquinone. By E. Schunck and H. Roemer (*Deut. Chem. Ges. Ber.*, **11**, 969—973).—A substance thus named by the authors, and isomeric with alizarin, is formed, together with anthraflavic acid and a third product to be described hereafter, by the action of sulphuric acid on oxybenzoic acid. It crystallises from alcohol, in which it is easily soluble, in yellow anhydrous needles, which melt at 291—293°, and burn with a bright flame. It is soluble also in acetic acid, benzene, ether, and chloroform, but not in water or carbon bisulphide. Sulphuric acid dissolves it, forming a brownish-yellow solution, which exhibits no absorption-bands. Potash, soda, and ammonia dissolve it with deep-yellow colour. Its barium derivative crystallises in long red needles. The calcium derivative is nearly insoluble. The substance combines with acetic anhydride to form the compound, $C_{14}H_6(C_2H_3O)_2O_4$, which crystallises in tufts of yellow needles melting at 199°. Metabenzdioxyanthraquinone, when heated with potash, yields purpurin. J. R.

Tetraphenylethane. By C. Engler (*Deut. Chem. Ges. Ber.*, **11**, 926—930).—Tetraphenylethane has hitherto been prepared (1) by reducing benzophenone with zinc-dust; (2) by the action of hydriodic acid and phosphorus on benzpinacone; (3) by the action of hydrochloric and zinc on benzhydrol in acetic solution; and (4) by the

action of hydriodic acid and phosphorus on benzpinacolin. The author describes the two following new methods of preparation, the former of which is suitable for preparing the body in large quantities.

1. The sulphuretted derivative of benzophenone melting at 151°, described by the author in a former paper (p. 61) (which may easily be obtained in any quantity) is dissolved to saturation in boiling alcohol, and the solution is boiled for some hours with an excess of copper precipitated from cupric sulphate by zinc. Cupric sulphide is thereby formed, and the whole of the benzophenone-compound is converted into tetraphenylethane, which is deposited from the filtered liquid, as it cools, in small acicular crystals, generally quite pure. The yield is about 94 per cent. of the theoretical amount. Or the benzophenone-compound may be heated with copper in the dry state, and the resulting tetraphenylethane sublimed in a wide-necked retort.

2. Benzophenone chloride (diphenyl-chloromethane), $(C_6H_5)_2CHCl$, obtained by passing dry hydrogen chloride into benzhydrol kept cool, is dissolved in benzene and boiled for some hours with sodium. The liquid on cooling, or after evaporation, deposits crystals of tetraphenylethane.

Tetraphenylethane is but sparingly soluble in alcohol. It dissolves more freely in ether and benzene, and very easily in carbon bisulphide and chloroform, from which last it is deposited in large crystals, on slow evaporation of the solution. With benzene it forms a crystalline compound, $C_{26}H_{22}.C_6H_6$, which is deposited from its solution in that liquid in well-formed transparent tables, turning opaque in the air.

A *sulphonic acid* of tetraphenylethane is formed on gently warming it with eight times its weight of concentrated sulphuric acid. The *barium salt*, $(C_{26}H_{18}(SO_3)_4Ba_2$, is very soluble. The free acid is soluble in water and alcohol, but scarcely in ether or chloroform. When fused with potash, it yields a phenol having the composition of *tetra-hydroxyl-tetraphenylethane*, and crystallising in laminæ, which melt at 248°.

A *nitro-compound*, $C_{26}H_{18}(NO_2)_4$, crystallising from aniline in small needles, is obtained by treating tetraphenylethane with nitric acid in the cold. By the action of tin and hydrochloric acid, it yields an amido-compound, the hydrochloride of which crystallises from water, and forms a crystallisable double salt with stannic chloride.

J. R.

Camphor. By F. Wreden (*Deut. Chem. Ges. Ber.*, **11**, 989).—On heating ordinary camphor at 190° with hydrochloric acid of sp. gr. 1·03 it is converted into an isomeric liquid modification, of sp. gr. 0·913. The liquid boils at 187—193°, and does not solidify at — 17°. It absorbs oxygen from the air, especially in sunshine, and gives no silver mirror with ammoniacal silver nitrate. J. R.

Reduction-products of Elemi-resin with Zinc-dust. By G. Ciamician (*Deut. Chem. Ges. Ber.*, **11**, 1344—1348).—This is a continuation of a previous investigation, undertaken to determine whether the different terpene-resins on reduction with zinc-dust, furnish similar products. The above resin was chosen because it could easily be obtained quite pure and crystallised. The products obtained were toluene, meta- and para-ethylmethyl-benzene and ethyl,

naphthalene. Those obtained previously from abietic acid and from colophony were toluene, ethylmethyl-benzene, naphthalene, methyl-naphthalene, and methylanthracene. Elemi-resin and abietic acid both yield toluene and ethylmethyl-benzene. Naphthalene and methyl-anthracene are not obtainable from elemi-resin, or at least in scarcely perceptible traces, and instead of the methylnaphthalene of the abietic acid, ethylnaphthalene is obtained from elemi-resin. In both cases toluene, ethylmethyl-benzene, and methyl- or ethyl-naphthalene, occur in far preponderating quantity, and it may therefore be inferred that the chemical constitution of these two substances is very similar.

W. S.

Splitting up of Cyclamin into Glucose and Mannite. By S. DE LUCA (*Compt. rend.*, **87**, 297—299).—The author shows that cyclamin, either coagulated or in aqueous solution, when left to itself for several months, splits up into two distinct substances, namely, glucose and crystallised mannite. Cyclamin must, therefore, be regarded as a glucoside, from which not only glucose, but also mannite, may be obtained.

R. R.

New Synthesis of Glycocyamine. By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], **17**, 477—480).—Glycocyamine is produced by the action of glycocine upon guanidine carbonate, in accordance with the equation $2C_2H_5NO_2 + (CN_3H_6)_2CO_3 = 2C_3H_7N_3O_2 + (NH_4)_2CO_3$. The aqueous solution of the two substances is boiled down to a small bulk, the glycocyamine is precipitated by addition of much water, and purified by repeating the same process three or four times. The glycocyamine obtained is identical with that of Strecker (*Compt. rend.*, **52**, 1212). The authors find that glycocyamine is soluble in 227 parts of water at 14·5°.

In the reaction of glycocine with guanidine carbonate, a substance is also produced which is possibly a double salt of the formula $C_2H_5NO_2.(CN_3H_6)_2CO_3.H_2O$. This substance separates in large clear rhombic tables from the warm saturated solution obtained by boiling down the original mixed liquids.

Guanidine carbonate reacts with amido-acids in general. The authors reserve the account of the compounds produced in this way for a future paper.

M. M. P. M.

Action of Iodic Acid, "Sulphomolybdic Acid," and Ferric Chloride on Morphine and other Substances. (*Pharm. J. Trans.* [3], **9**, 70).—Morphine hydrochloride dissolved in water, strikes a transitory blue with starch and iodic acid. With grape juice and starch, iodic acid produces no blue; but a dirty blue is observed with the alcoholic extract of the dried juice. Orange-juice, with starch and iodic acid, gives instantly a blue colour. Saliva also produces a bright blue; but a mixture of orange juice and saliva produces a violet colour. This reaction resembles that of morphine, but there is no alteration of the colour, the blue not being produced. With sulphomolybdic acid, morphine gives a purple colour, which rapidly disappears, the liquid becoming brown, and finally blue. With grape juice no coloration appears for nearly half-an-hour. Fresh orange juice remains unaltered, but with the dried juice, a faint blue is visible in

ten minutes. The same result is obtained with saliva. When saliva and orange juice are mixed, coloration ensues only after the lapse of half-an-hour. Ferric chloride produces a bluish-green with morphine, whereas a red is produced with dry or wet saliva; but no result is obtained with orange juice and saliva. A wine-red tint is perceptible with the twelve-thousandth of a grain of meconic acid in presence of ferric chloride. E. W. P.

Remarks on Rice's Articles on the Cinchona Alkaloïds. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1549—1560).

Substitutes for Quinine. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1546—1549).—Dita bark (the bark of *Alstonia scholaris* or *Echites scholaris*) contains two alkaloïds, *ditamine* and *echitamine*. Gruppe's extract of dita bark, ditaine, acts like curare; this is probably due to the echitamine.

The bark of *Alstonia spectabilis*, which is also used as a febrifuge, contains the alkaloïd *alstonamine*.

The bark of *Crossopteryx Kotschyana* (syn. *Crossopteryx febrifuga*) contains 0·018 per cent. of the alkaloïd *crossopterine*, but does not contain quinine.

Crossopterine is soluble in alcohol, ether, and hydrochloric acid. It is precipitated from the hydrochloric acid solution by ammonia, soda, platinum chloride, and by the double iodide of potassium and mercury. W. C. W.

Cinchonine and Cinchonidine. By Z. H. Skraup (*Deut. Chem. Ges. Ber.*, **11**, 1516—1519).—The results of numerous analyses of cinchonine and its salts are given in support of the author's view, that the composition of cinchonine is $C_{19}H_{22}N_2O$, and not $C_{20}H_{24}N_2O$. Cinchonine generally contains small quantities of the compound $C_{19}H_{24}N_2O$ (the hydrocinchonine of Willm and Caventou), to which the name *cinchotine* is given by the author. The two bases may be separated by fractional crystallisation of the mixed sulphates or tartrates. Cinchotine sulphate crystallises in prisms containing $11\frac{1}{2}$—12 molecules of water. It is slowly attacked by potassium permanganate in the cold. Dihydrodicinchonine sulphate is easily distinguished from the preceding compound by forming long slender crystals, containing 2 molecules of water, and by being readily attacked by potassium permanganate.

Cinchonine is oxidised by potassium permanganate, forming formic acid and cinchotenine.

Cinchonidine has the same composition as cinchonine, viz., $C_{19}H_{22}N_2O$, and is considered by the author to be probably identical with homocinchonidine. On oxidation, cinchonidine yields formic acid and a lævo-rotatory body (m. p. 256°), which is an isomeride of cinchotenine. It is proposed to call this substance *cinchotenidine*.

W. C. W.

Remarks on the preceding Paper. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1520—1521).—The author publishes the results of several analases in favour of the formula, $C_{20}H_{24}N_2O$, for cinchonine,

and gives a test for distinguishing cinchonidine sulphate from homocinchonidine sulphate, viz.: 1 part of the substance is dissolved in 50 parts of warm water, and left at rest for two hours. Cinchonidine sulphate crystallises out in long brilliant prisms, whilst homocinchonidine sulphate forms groups of delicate dull-white prisms. This test cannot be used in presence of appreciable quantities of quinine.

W. C. W.

A New Organic Base in Animal Organisms. By P. Schreiner (*Liebig's Annalen*, **194**, 68—84).—Charcot and Robin and numerous other observers have remarked the occurrence of a peculiar crystalline body in the secretions and in certain organs of the animal organism. The crystals, which appear to be especially plentiful in patients suffering from bronchial asthma, or from leucocythæmia, were supposed by Friedrich and Huber to be tyrosine. Harting believed them to be calcium phosphate, Böttcher albuminoïd bodies, and Salkowski and Forster regarded them as mucous compounds. The author has shown that this body is the phosphate of an organic base. The crystals form 5·237 per cent. of the solid constituents of human semen, and can be easily obtained by boiling the fresh fluid with alcohol, treating the precipitate, after it has been dried at 100°, with warm water, containing a few drops of ammonia, and evaporating the alkaline solution. The crystals also separate out on the surface of pathological preparations which are preserved in alcohol. After purification by recrystallisation from hot water containing a small quantity of ammonia, the crystals (prisms and double pyramids) are colourless and brittle. They are insoluble in ether, chloroform, alcohol, and in cold water, but they dissolve readily in dilute acids, in solutions of caustic alkalis and alkaline carbonates.

The salt contains two atoms of nitrogen to one of phosphorus; it loses 3 mols. of water at 100°, melts at 170°, and decomposes at a higher temperature, giving off ammonia. By precipitating the phosphoric acid with baryta-water, the free base is obtained as a colourless, inodorous crystalline mass, having a bitter taste. It is soluble in alcohol, insoluble in ether, and its solution immediately forms a crystalline compound on the addition of phosphoric acid. The base has been extracted from the liver, spleen, lungs, and blood of cattle, and from the liver, spleen, blood and marrow of men who had suffered from leucocythæmia, by boiling with water containing acetic acid. Lead acetate was added to the solution, the excess of lead removed from the filtrate by means of sulphuretted hydrogen, and the base precipitated by phosphotungstic acid. The free base, obtained by boiling the phosphotungstate with baryta, forms a crystalline compound with hydrochloric acid, $C_2H_5N.HCl$. On the addition of platinum chloride to the hydrochloride, large prismatic crystals slowly separate out. Gold chloride precipitates the compound $C_2H_5N.HCl.AuCl_3$, which crystallises in golden plates, soluble in ether, alcohol, and in water. The characteristic odour of fresh human semen is observed, when an aqueous solution of the gold salt is treated with metallic magnesium.

W. C. W.

Lotur Bark. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1542—1546).—Lotur bark, the bark of *Symplocos racemosa*, contains three alkaloïds, viz.: *loturine*, 0·24 per cent.; *colloturine*, 0·02; and *loturidine*, 0·06 per cent. The alkaloïds are extracted from the bark by hot alcohol, and are converted into acetates. Loturine and colloturine are precipitated from the neutral solution by the addition of potassium thiocyanate, leaving the loturidine in solution. The crystalline precipitate is decomposed by soda, and the alkaloïds are extracted with ether and recrystallised from alcohol. The efflorescent crystals of loturine are separated mechanically from the non-efflorescent crystals of colloturine.

Loturine is soluble in alcohol, ether, chloroform, and acetone, but is insoluble in water, ammonia, and caustic soda. It gives no coloration with ferric chloride, strong sulphuric or nitric acids, or even on the addition of bleaching powder and ammonia. Loturine melts at 234°, and sublimes, forming colourless prisms. The fluorescence exhibited by a solution of loturine in dilute acids is more intense than that of quinine sulphate. Loturine forms well-crystallised salts. The hydrochloride, which crystallises in white prisms soluble in alcohol and in water, forms double salts with the chlorides of platinum, gold, and mercury. The hydriodide forms a crystalline double salt with mercuric iodide. The nitrate, thiocyanate, acetate, chromate, and picrate are crystalline compounds. The tannate and phosphotungstate are amorphous powders.

Colloturine is deposited from alcohol in prisms terminating in pyramids, which sublime at 234°. The solution of the alkaloïd in dilute sulphuric or hydrochloric acid is fluorescent. Gold chloride produces a yellow amorphous precipitate in the solution of the hydrochloride.

Loturidine.—The filtrate from the thiocyanates of loturine and colloturine is rendered alkaline by ammonia, and the loturine extracted with ether. Loturidine is a yellowish-brown amorphous body yielding amorphous salts. It dissolves in strong nitric and sulphuric acids forming yellow solutions. The solution in dilute acids is fluorescent.

Winckler's *californine* was not a simple substance, but a mixture of the acetates of these three alkaloïds. W. C. W.

Amyrin and Icacin. By O. Hesse (*Liebig's Annalen*, **192**, 179—182).—The author compares the analyses of these two substances, and is inclined to regard icacin and amyrin as hydroxyl-compounds, viz.: $C_{47}H_{77}.OH$ and $C_{47}H_{76}(OH)_2$ respectively. No new experimental data are given. M. M. P. M.

Composition of the Milk of the Cow-tree. By Boussingault (*Compt. rend.*, **87**, 277—281).—The author has recently analysed the juice of the cow-tree (*Brosimum galactodendron*) which is used in South America as an article of diet. The results show that this vegetable milk, in its general composition, has much resemblance to that of the cow, inasmuch as it contains a fatty substance, saccharine matters, casein, albumin, and phosphates. The proportions of these substances in the juice of *Brosimum galactodendron* are, however, such

that it must be regarded as resembling cream rather than milk, as the following figures will show:—

Juice of B. Galactodendron.		*Cream.*	
Wax and saponifiable matter	35·2	Butter	34·3
Saccharine substances	2·8	Milk sugar	4·0
Caseïn, albumin, phosphates, &c.	4·0	Caseïn and phosphates	3·5
Water	58·0	Water	58·2
	100·0		100·0

The fatty substances in the vegetable milk, according to C. Bernard, are capable of being split up into fatty acids and glycerin.

R. R.

Physiological Chemistry.

Influence of the Temperature of the surrounding Atmosphere on the Excretion of Carbonic Acid and the Absorption of Oxygen in a Cat. By the Duke Carl Theodor of Bavaria (*Zeitsch. f. Biologie*, **14**, 51—56).—In this series of experiments the author fed a full-grown cat on a fixed diet from December 14th, 1874, to Jan. 14th, 1875. For the first 17 days the cat received daily 100 grams of beef and 10 grams of pure lard, but as the animal was losing weight the diet was increased to 120 grams of meat and 15 grams of lard; this was continued throughout the experiments. Except when placed in the respiration apparatus, the animal was kept in an unheated space, and was therefore exposed to the variations in temperature of the climate (Munich). The cat was weighed daily and the average temperature of the air noted. From December 31st to June 16th the animal increased somewhat in weight; from the latter date to March 30th (*i.e.*, during the cold season of the year) its weight remained nearly stationary (between 2,557 and 2,650 grams). With the advent of warm weather, however, it gradually increased in weight, until on June 14th it weighed 3,047 grams.

The author thence concludes that, for some reason less nourishment is required during summer than in winter, for the same diet which during the cold weather merely maintained the animal at its original weight, caused a considerable increase in the same during the summer.

During the above-mentioned six months, 22 experiments, each lasting from five to six hours, were made with the respiration apparatus, the absorption of oxygen, as well as the excretion of carbonic acid and watery vapour, being estimated. The experiments were made in each case after the cat had fasted 17 hours.

The results showed plainly that the excretion of carbonic acid and the absorption of oxygen are increased by cold and diminished by heat. The fact that the numbers do not increase uniformly with the

lowering of the temperature, the author attributes to movements of the cat sometimes taking place, whereas the animal usually remained quiet in the apparatus. The average proportion of the oxygen absorbed to that contained in the carbonic acid excreted was as 100 : 77, being the same as that found in the fasting dog. E. C. B.

Influence of the Temperature of the surrounding Air on the Processes of Decomposition in the Organism of Warm-blooded Animals. By C. Voit (*Zeitsch. f. Biologie*, **14**, 57—160).—This lengthy paper is divided into numerous sections, of which the first treats of the literature of the subject, and the others are as follows:—

2. *Experiments with a cat.*

3. *Experiments on man in cold and heat with exclusion of voluntary movements.*—The results obtained showed that both in the case of the cat and of man, when the temperature fell below the ordinary (14—15° C.), the excretion of carbonic acid was increased, the increase amounting in man to 36 per cent. in a fall of 9·9°. Increase of temperature on the contrary does not show a gradual decrease, but also a slight increase in the carbonic acid, which amounted to 10 per cent., when the temperature was raised 15·7°. There is therefore, the author concludes, no doubt that it is not the voluntary movements which give rise to the increased excretion of carbonic acid.

4. In this section, the author traces the gradual development of the theory of the decomposition of albumin, fats, and carbo-hydrates, not by the direct action of oxygen, but by means of organised ferments. He does not consider the temperature as the immediate cause of the decomposition, and cites the case of the diabetic (in whom, under certain circumstances, there may be a large consumption of oxygen), to show that temperature and oxygen together do not suffice to bring about the decomposition of the sugar. In diabetes, causes which normally bring about the decomposition of sugar are absent, on which account little oxygen is usually absorbed.

5. *Influence of the Respiratory movements on the formation of Carbonic acid.*—According to the author the influence of the respiratory movements on the formation of carbonic acid and on the decompositions taking place in the body is due, not to the different quantities of oxygen inhaled, but to the increased muscular activity under these circumstances.

7. *Experiments on the Marmot during Hibernation.*—Two experiments made by the author in 1874 confirm previous observations, showing that glycogen exists in the liver in large quantities in hibernating marmots. This indicates, he thinks, that glycogen is formed in the fasting organism, although this cannot usually be proved; in the waking state there must be some cause which brings about its immediate decomposition. This cause he considers to be the muscular movements of the waking animal.

8. *Consumption of Oxygen in Man during Sleep.*—Experiments by the author and Pettenkofer, made in 1866, seemed to show that during the night considerably more oxygen is absorbed than during the day, and also that during the day considerably more oxygen is excreted in the products of decomposition than is absorbed in the mean time. The

author now detects an error in some of these experiments, owing to the increase in weight of the bedding (due to absorption of moisture from the air) in 24 hours, being all attributed to the 12 hours of the night; the excretion of water found during the day was therefore too little, that during the night too great, rendering the calculated amount of oxygen absorbed during the day too small, that for the night too great.

9. In an experiment on a fasting dog during a sleep of 4 hours 25 minutes, induced by chloral, the author found that very little carbonic acid was given off and very little oxygen absorbed, but, whereas during hibernation the amount of oxygen absorbed was much greater than that excreted, in this case the difference was abnormally small.

10. An experiment made on a man suffering from paralysis, after fracture of the eighth dorsal vertebra, gave for 12 hours an excretion of carbonic acid amounting to 250 grams, being 38 per cent. less carbonic acid than that excreted during the 12 hours of the day by a man in health, and 20 per cent. less than that given off during the 12 night hours. The author concludes from this and other observations that the stimuli acting on the organs of sense exert by means of the nervous system a continual stimulating influence on the decompositions taking place in the organism. The nerves are not, he considers, the cause of the decomposition, but they exert a modifying influence on this cause, and are able to bring about conditions more favourable to the same.

12. *Decomposition of Fat can be increased by Reflex action.*—The decomposition of albumin is dependent chiefly on the amount of albumin carried to the living cells, that of the fat, on the other hand, on the change in relation of the particles brought about by nerve influence. Experimenting on dogs rendered motionless by curare, the author finds that, as during sleep, much less carbonic acid is excreted, which he attributes not to a diminution of the amount of albumin decomposed, but to a less decomposition of fat. From these observations, he considers it probable that cold or other stimuli acting on the skin, and also light, when they cause in a reflex manner an increase in the excretion of carbonic acid and absorption of oxygen, do so merely by increasing the decomposition of the non-nitrogenous substances and not that of albumin. Lowering of the surrounding temperature, as long as the temperature of the body remains constant, he finds only brings about an increased decomposition of fat or non-nitrogenous substances. When, however, the body-temperature is reduced, there is probably a diminution in the decomposition both of albuminous and of non-nitrogenous substances. Increased body-temperature artificially produced, or the result of fever, is accompanied by an increased decomposition of albumin; it is doubtful whether the decomposition of fat is also increased.

13. The increased decomposition in the cold due to involuntary regulation is not, the author considers, of very much importance to life in cold climates, for it is assisted by other more efficient means, viz.: by clothing the body with bad heat-conductors, by production of much heat, by a great consumption of nourishment, and by muscular action.

In man and in the cat, he considers that there does not exist for higher temperatures any appreciable reflex regulation by diminished oxidation. E. C. B.

Magnesia as an Antidote for Arsenious Acid. By P. de Clermont and J. Frommel (*Compt. rend.*, **87**, 332).—In seeking to eliminate arsenious acid in the experiments referred to on page 13 of this volume, the authors found that on adding magnesia to water holding sulphide of arsenic in suspension, two combinations are formed: a sulph-arsenite of magnesium, $Mg_3(AsS_3)_2$, which is soluble in water, and an arsenite, $MgHAsO_3$. insoluble. The equation representing this reaction is :—$2As_2S_3 + 5MgO + H_2O = Mg_3(AsS_3)_2 + 2MgHAsO_3$. The soluble sulph-arsenite is dissociated when boiled, thus :—$Mg_2(AsS_3)_2 + 7H_2O = MgHAsO_3 + 6H_2S + MgO$. Magnesia is an excellent antidote in cases of poisoning by arsenious acid, as the arsenite is completely insoluble; but supposing that a portion of the arsenious acid becomes converted into trisulphide in the stomach or intestines, the magnesia would render this soluble. Now, in the intestines of a person poisoned by arsenious acid, trisulphide in the state of fine yellow powder has been observed (*Neu. Reper. der Pharm.*, **17**, 386); and the question arises whether magnesia is as efficacious as has been supposed, seeing that the sulphide which would otherwise not be capable of absorption, is rendered soluble by it. R. R.

Analytical Chemistry.

Colorimetric Experiments. By J. Bottomley (*Chem. News*, **38**, 191—193).—Experiments were made to determine, if possible, the amount of colouring matter in a liquid by comparison with a standard liquid. White disks were sunk in two equal cylinders, the one containing the standard liquid, the other that to be tested, it being thought that the depth of the disk would be inversely as the quantity of the colouring matter present. It appears, however, that the method cannot be practically employed, owing mainly to the difficulty of detecting the exact shades of colour. E. W. P.

Schutzenberger's Process for the Volumetric Estimation of Oxygen in Water. By C. C. Hutchinson (*Chem. News*, **38**, 184—187).—In water containing sewage, oxygen is present in quantities below the normal, but the quantity increases as the sewage decreases; in deep well-water, however, containing no sewage, it is stated there is an almost total absence of oxygen; this may be owing to its having already been removed by organic matter during its passage through the strata. To settle the question whether oxygen is or is not an indication of the purity of water, the author was anxious to employ some method more rapid than that of Bunsen's for the determination of the amount of oxygen present, but it appears by the experiments that the method which he proposed to employ is scarcely accurate enough, although it admits of great rapidity, and is more suited for a small quantity than for a large quantity of water: it is also valuable as a preliminary experiment. The method consists in

adding a known volume of the water to a solution capable of being oxidised, accompanied by a change of colour, by the oxygen contained in the water. The extent to which this has occurred is then determined by the addition of a reducing agent, which reduces it to its former condition. This last solution is standardised in terms of the oxygen it is capable of taking up; and from the amount used in the experiment, the volume of oxygen present is calculated. The reducing agent employed is sodium hyposulphite, made by passing sulphurous anhydride to saturation into a solution of soda, sp. gr. 1·4, diluted to sp. gr. 1·34, and reducing the product with powdered zinc: milk of lime is then added, which precipitates the zinc and also renders the liquid less absorbent of free oxygen. The liquid by which the change of colour detects the completion of the process is either sodium sulphindigotate, or Coupier's aniline blue; 10 grams of the indigotate are dissolved in 1 litre of water. An ammoniacal solution of copper sulphate containing 4·46 grams per litre is used to standardise the above solutions. The estimations must all be made in an atmosphere of hydrogen. The process for determining the oxygen present is fully described, as well as the method of standardising the solutions. E. W. P.

Appendix to the Estimation of Carbonic Acid in the Air. By W. Hesse (*Zeitschr. f. Biologie*, **14**, 29—33).—Having given some additional directions with a view to avoid the introduction of carbonic acid from the outer air along with the baryta-water, the author recommends the following method for ordinary purposes:—A solution of oxalic acid of ·5727 gram to the litre is prepared, and baryta-water, of which 10 c.c. neutralise from 20 to 25 of this solution of oxalic acid, and volumes of air of about half a litre are used. According to whether 4 to 5 per mil. or more of carbonic acid are expected, 10 to 20 c.c. of baryta-water are added. The pipette is inserted through an india-rubber stopper with two perforations, the escape of air from the flask being regulated by the finger on the second aperture. The flask is rapidly closed after removing the pipette. The numbers are often somewhat too high. E. C. B.

Quantitative Determination of Sulphur in Illuminating Gas. By Poleck and Biefel (*Chem. Centr.*, 1878, 331).—A measured quantity of the gas to be examined is burned in air, and the products of the combustion drawn through an alkaline solution of bromine by means of a water aspirator. The sulphur is determined as barium sulphate. The gases examined by the authors were taken from the works at Breslau, the experiments being made on the same day, and as rapidly one after the other as possible. The following results were obtained:—

	Sulphur in 1,000 litres of gas.
In the retort house.....	0·600 gram
Before the scrubbers	0·540 „
After passing the scrubbers	0·464 „
After passing the condensers ..	0·440 „
In the finished gas.....	0·276 „

In the first four determinations, H_2S is included; and when CS_2 is

separately determined in the finished gas, the residual sulphur may be considered as belonging to the so-called sulphuretted hydrocarbon, the smell of which resembles phenyl mustard-oil. J. M. T.

Estimation of Nitric Acid as Ammonia. By E. A. Grete (*Deut. Chem. Ges. Ber.*, **11**, 1557—1558).—Nitrates are completely reduced to ammonia by heating to redness with soda lime and a xanthogenate. W. C. W.

Estimation of Nitrous and Nitric Acids. By G. Lunge (*Dingl. polyt. J.*, **228**, 447—450).—Lunge has constructed an apparatus for determining the above acids, which is a modification of Watts' apparatus described by Davis (*Chem. News*, **37**, 45), and resembles Bunte's modification of Rauch's gas burette. This improved form has no trough, and requires but little more mercury than is necessary to fill the tube (about 850 grams); it is easily cleaned out after every operation, and has the advantage of the mercury not coming into direct contact with the worker. Lunge calls it a "nitrometer." D. B.

Behaviour of Quartz with Microcosmic Salt. By E. Laufer (*Deut. Chem. Ges. Ber.*, **11**, 935).—In a former paper, the author described a method of separating quartz from admixtures with silicates by fusion with microcosmic salt, which it was then thought decomposed silicates without attacking quartz. But further experiment has shown that the method cannot be relied upon, inasmuch as quartz itself, especially when finely powdered, is acted on by the fused salt. J. R.

Testing and Valuing Gas Liquor. By T. H. Davis (*Chem. News*, **38**, 193—195).—Gas liquor, or a crude solution of ammonia salts, is generally sold on the basis of its sp. gr., or on its degree (Twaddle). This test is, however, untrustworthy, although an indication of the "strength" of the liquor is obtained. Now, as the ammonia is that for which the manufacturer contracts, it is recommended to titrate the liquor as follows:—Into a flask of about 300 c.c. capacity 10 c.c. of the sample to be tested are run in, and into this 15 c.c. of normal sulphuric acid. The contents of the flask are then raised to boiling, a few drops of litmus added, and titrated back with normal soda. The number of c.c. of soda used are deducted from the 15 c.c. of acid employed, the result multiplied by 17, and divided by the specific gravity of the liquor. The result thus obtained represents the percentage of ammonia contained in the liquor. E. W. P.

Remarks on the Estimation of Calcium Sulphate in Beer. By H. M. Wilson (*Chem. News*, **38**, 197).—Organic matter appears to interfere with the complete precipitation of the sulphuric acid in beer as barium sulphate. It is advisable, therefore, in the first instance to evaporate 100 c.c. of the sample to dryness, and after the addition of 0·5 gram potassium nitrate, to ignite the residue. E. W. P.

Presence of Lead in Bismuth Subnitrate. By CHAPIUS and LINNOSSIER (*Compt. rend.*, **87**, 169—171).—Carnot has shown that all samples of bismuth subnitrate of commerce contain lead, sometimes in quantities dangerous for public safety. The authors of the present paper propose the following method for the quantitative detection of the lead. The bismuth nitrate to be examined is boiled with caustic soda and a small quantity of potassium chromate, the residue, after boiling, being thrown upon a filter. To the filtered liquid, acetic acid is added until the solution is just acid, when a yellow precipitate is produced, more or less pronounced, according to the amount of lead present. For $\frac{1}{100}$ an abundant precipitate is obtained; for $\frac{1}{1000}$ the cloudiness of the liquid is distinct, and a deposition very soon takes place in the form of a precipitate adhering to the sides of the tube; $\frac{1}{5000}$ shows only slight cloudiness, often appearing only on cooling, as lead chromate is slightly soluble in the mixture of sodic acetate and acetic acid; smaller quantities could be detected if the weight of substance used was increased.

After mentioning that both calcium phosphate containing silica or alumina, and also impure soda interfere with the reaction, he describes the following quantitative method similar to that described for the qualitative detection.

About 10 grams of the bismuth nitrate are used, care being taken to wash the chromate of bismuth with a mixture of potassium chromate and sodium hydrate, first by decantation, and then on the filter until the filtrate is no longer rendered turbid by acetic acid in excess. The filtrate is now boiled, supersaturated with acetic acid, allowed to stand 24 hours, and filtered. The precipitate is then washed with water slightly acidulated by acetic acid, dried at 100° and weighed. The weight found, multiplied by 0·6408, gives the weight of lead contained in the 10 grams of substance. J. M. T.

Estimation of Nitrogen in Organic Bodies. By E. A. GRETE (*Deut. Chem. Ges. Ber.*, **11**, 1558).—In estimating the nitrogen in horn, leather, and wool refuse, the author advocates dissolving the substance in warm concentrated sulphuric acid before heating with soda-lime. Higher results are obtained than by the ordinary process. W. C. W.

New and Rapid Process for the Analysis of Milk. By A. ADAM (*Compt. rend.*, **87**, 290—291).—The analysis is performed by means of an apparatus consisting essentially of a glass tube of about 40 c.c. capacity, provided with a stopper at the top, expanded in the middle, and tapered off at the bottom, which is closed by a glass stopcock. Into this apparatus is introduced 10 c.c. of alcohol of 75°, containing $\frac{1}{200}$ of its volume of sodic hydrate; then 10 c.c. of milk, which must be neutral; and finally, 12 c.c. of pure ether. The liquids are shaken together, and allowed to remain at rest for five minutes, when they separate into two layers: the clear upper one contains all the butter; the lower, the lactose and caseïn. The butter contained in the former is estimated by evaporating and weighing, allowing 1 centigram for a little caseïn, &c., which may be con-

tained in the liquid, or eliminating this by re-solution in ether. In the liquid first drawn off, the lactose and caseïn are estimated by making up to 100 c.c. with distilled water, and adding 10 drops of acetic acid; the caseïn then separates, and after having been removed by filtration, is pressed between folds of bibulous paper, dried, and weighed. The filtrate contains the salts of the milk, the acetate of sodium formed, and the lactose. The latter is estimated by means of Fehling's cupro-potassic liquid. All these operations are easily performed in an hour and a half; and if, at the commencement, 10 c.c. of the milk acidulated with two drops of acetic acid are set to evaporate, the weights of dry residue, ash, and water may be obtained within the same time. R. R.

Butter Analysis. By H. Hager (*Chem. Centr.*, 1878, 333—334). —I. 20·0 parts of the butter to be analysed, together with 3·0 to 4·0 parts of pure sodium chloride, are placed in a weighed glass vessel, and the whole is weighed and heated to 50—80° in a water-bath, when the fatty part forms a yellowish layer on the top, whilst the water, caseïn, and salt remain at the bottom. Two portions of 5·0 parts of the clear fat are placed in glass flasks of about 12·0 c.c. for further investigation, as described in III.

II. *Estimation of Moisture, Caseïn, and Salt.*—The fat is decanted as far as possible; then 10 c.c. of warm benzene are added and gently agitated with the liquid, so as to take up the rest of the fat. The vessel is then allowed to stand in a warm place for half-an-hour, when the benzene is poured off and 10 c.c. more are added to remove the last traces of fat. The liquid is allowed to stand for half-an-hour longer in a warm place to remove the last traces of benzene, and the vessel and its contents are again weighed; this, after subtracting the 3·0—4·0 NaCl added, gives the weight the total moisture, caseïn, and salt. The residue is then treated with hot water and filtered. The filtrate evaporated to dryness gives, after subtracting the NaCl added, the salt in the butter. The casein remains on the filter.

III. *Saponification of the Butter Fat.*—To the 5 grams of fat in the flask, 20 c.c. of alcohol are added, and 10 c.c. of a freshly-prepared solution of 2·0 grams of pure caustic soda in 10·0 of distilled water; the whole is then agitated and heated to 50—60°, when the flask is corked and violently shaken. The alcohol prevents frothing. After a few moments' rest, small particles of fat are observed if the saponification is not complete. When this is the case, the flask is uncorked and again heated; recorked, wrapped in a towel, and shaken; it is scarcely ever necessary to repeat the operation a third time. The author says that it takes about 6—8 minutes for complete saponification.

IV. The warm soap-solution is poured into a large beaker, and the flask washed out with 45 per cent. alcohol. The solution is then warmed without boiling, so as to evaporate as much as possible of the alcohol; 3—4 c.c. do not interfere with the following reactions. A little warm water is added, and then 20·0 of previously warmed dilute sulphuric acid (1 : 5 water), and stirred; water is then poured in until the level of the liquid is about 2 c. below the mouth of the beaker. After the fat has completely separated out in the water-bath or other

warm place, 5·0 of perfectly dry white wax or paraffin are added, heated to melting, and the whole placed in a cool place to solidify, leaving the glass rod in a beaker. The evaporation of the alcohol is necessary on account of the solubility in an alcoholic solution of the fatty acids insoluble in water.

V. As the fatty acids soluble in water require a large quantity of the latter, it is better to employ 20—23 per cent. alcohol, as it dissolves them readily without acting on the insoluble acids. After cooling, the glass rod, with the cake of fat adhering to it, is carefully lifted out, the water poured off and replaced by the alcohol described above, and the fat again put into the beaker and gently boiled for about eight minutes. After cooling, the liquid is poured off and the whole operation repeated, when all the soluble fatty bodies will have been removed.

VI. The cake is now dried by means of blotting paper, and removed from the rod into a small flat-bottomed dish, previously weighed, together with the particles of fat which may have adhered to the beaker; dried at 100—120°, and weighed, the weight of the wax added being subtracted.

VII. It is safe to assume that butter fat contains 88 per cent. of fatty acids insoluble in water. When the amount of acid found does not exceed 88 per cent., nothing but pure butter fat is present. When it is between 88 and 89, the butter fat may have been adulterated with other fats. When this is the case, a wick should be impregnated with the fat, lighted, and blown out. If the well-known smell of a tallow-candle is not distinctly perceived, the butter may be considered to be quite pure. When the weight exceeds 89 per cent., the butter is certainly adulterated. J. M. T.

Adulteration of Wine. By F. v. Lepel (*Deut. Chem. Ges. Ber.*, **11**, 1552—1556).—Beetroot juice is used in colouring wines for the purpose of concealing the presence of "magenta." The absorption-bands of "magenta" are hidden by those of the beetroot; but if a few drops of copper sulphate solution are added to the wine, the beetroot-bands gradually vanish, and the "magenta" spectrum becomes visible.

To detect "magenta" in presence of an extract of the flowers of the wild poppy, *Papaver Rhœas*, 1 drop of iodine solution (·01 gram per c.c.) is added to the wine, before examination with the spectroscope. W. C. W.

Detection of Wines Adulterated with Grape Sugar. By C. Neubauer (*Dingl. polyt. J.*, **229**, 463—466).—After decolorising the wine, which, when examined in tubes 220 mm. long with Wild's large polaristrobometer, shows a slight dextro-rotation of 0·4 to 0·6° (1° Wild = 4·6043° Soleil = 2·89005° Ventzke-Soleil), 250 to 350 c.c. are concentrated until the salts begin to crystallise out. The concentrated solution is, after the addition of a sufficient quantity of pure animal charcoal, diluted to 50 c.c., and filtered. The filtrate, generally of a faint yellow colour, shows with most wines a slight dextro-rotation in tubes 220 mm. long, which varies with pure Rhine, Haardt, and Markgräfler-wines, from the years 1874 to 1876 between 0·5 and 2°. The 50 c.c. are next evaporated to a

syrupy mass on the water-bath, the residue being treated gradually and with careful stirring with a quantity of 90 per cent. alcohol, large enough to throw down all precipitable matter. After having allowed the mixture to stand for 6 to 8 hours, the alcohol is either poured off or filtered off, and the residue extracted with cold water. The solution is decolorised with animal charcoal and filtered. In all natural wines the dextro-rotatory substance is chiefly in this alcoholic precipitate. The alcoholic filtrate is evaporated to one-fourth of the volume originally added, and the cold solution treated gradually with four to six times its volume of ether, shaking the mixture the whole time. After standing, a more or less thick aqueous solution separates under the ether, which in wines containing potato-sugar contains the non-fermentable substances of these preparations, soluble in alcohol (amylin), and consequently shows a strong dextro-rotation. After removing the ether, the aqueous solution is diluted with water, warmed on the water-bath, to expel all ether, decolorised with animal charcoal, and the filtrate diluted according to the size of the observation-tube to the necessary volume. With pure natural wines of medium growths, which no longer contain unfermented sugar, the dextro-rotation of this aqueous solution of the ether precipitation from 250 to 350 c.c. of wine is, after discoloration and dilution to 30 c.c. either nil, as in most cases, or at the most, 0·2° to 0·5°. The tables given in the original paper show that all wines having a rotation of 0·1° to 0·3° to the right, may be regarded as perfectly pure. If, however, the dextro-rotation is 0·5° to 0·6°, it is more satisfactory to apply the above-described method. D. B.

Alizarin Colouring Matters, and Green Aniline Colours. By H. W. Vogel (*Deut. Chem. Ges. Ber.*, **11**, 1371—1374).—*Alizarin-blue.*—This body dissolves in water on addition of ammonia with indigo-blue colour, and shows a two-sided absorption of the spectrum, which appeared considerably stronger in the red than in the dark blue, and no bands could be recognised. Supersaturated with nitric acid, the solution becomes brick-red, and exhibits an absorption similar to that of red litmus tincture with a dark shadow in the green. Amyl alcohol extracts the colouring matter quickly from the acid solution, but only with difficulty from the alkaline solution. Alcohol dissolves the colouring matter in the completely neutral condition, with violet colour. Treated with ammonia, the solution becomes blue, like cupric sulphate solution, and exhibits in the concentrated state a continuous absorption of the red end of the spectrum, and on diluting with alcohol, a highly characteristic spectrum reaction for alizarin-blue is developed. This consists of three bands, the weakest of which is on D, the second between *d* and C (daylight), and the third on the extreme limit of the red, and is perceptible only with the strongest lamp-light. Potash acts differently on the alcoholic alizarin-blue solution. It becomes of a beautiful green, and then absorbs on both sides, most strongly at the red end of the spectrum, but without bands. The aqueous solution gives the same reaction. As regards detecting the colouring matter, it is best to warm the coloured fabric with dilute

hydrochloric acid, extract the colouring matter with amyl alcohol, and treat this with alcohol and ammonia.

Alizarin-orange (nitro-alizarin) in alcoholic solution shows a strong extinction of the blue, and a weaker one of the green. With certain degrees of concentration two very indistinct bands are recognised in the green. With ammonia the solution becomes coloured reddish, and then shows a stronger absorption of the green. With nitric acid it becomes bright yellow, and gives a one-sided absorption of the blue. Potassium hydroxide colours the alcoholic solution a beautiful rose colour, and gives then a continuous extinction of the green from F to D, in which two bands appear. Aqueous solutions of the colouring matter with potash become yellowish-red, and show a homogeneous shade without bands in the green. The acid aqueous solution of the "alizarin-orange" is easily extracted with amyl alcohol, and then gives with alcohol and potash a definite spectral reaction. From coloured textures, it is extracted just as "alizarin-blue" is.

Both "iodine-green" and methylrosaniline picrate show in dilute alcoholic solution an absorption-band between *d* and C. "Iodine-green" shows further a weak band on the D line, which disappears on dilution. The concentrated alcoholic solutions of both colours diluted with water turn their absorption-band somewhat towards the green (difference from "aldehyde" and "malachite-green"). A drop of nitric acid added to the alcoholic solution of the "iodine-green" effects no alteration in the bands (difference from "aldehyde-green"). The green picrate is turned bluer with nitric acid, and the bands widen towards the green. A drop of ammonia colours "iodine-green" solution violet, with formation of a band on the D line. The green picrate does not show this reaction; it becomes yellowish. By addition of ammonia to the nitric acid solutions of the colouring matter, the original colour and the spectral bands gradually return.

Malachite-green, in its optical behaviour, exhibits striking resemblance to "aldehyde-green," but differs from it in its chemical properties. The former dissolves much more easily in alcohol, and the solution appears bluer than that of "aldehyde-green." Dissolved in alcohol and suitably diluted, both give exactly the same spectrum. In highly dilute solutions, one band appears on the *d* line, widening itself in concentrated solution, and besides, a continuous absorption of the blue. The only difference between the two colours is that the "aldehyde-green" weakens the red right and left from the absorption-band somewhat more strongly than "malachite-green;" with the latter, the band appears, on the other hand, considerably darker. Although so similar in optical properties, the two colours differ decidedly in their behaviour with acids. A drop of hydrochloric acid or nitric acid added to the alcoholic "aldehyde-green" effects no apparent alteration of colour; on the contrary, in the nitric acid solution a striking alteration of position of the absorption-band to the right is remarked, whilst the band of the "malachite-green" does not suffer the least alteration. With ammonia, "malachite-green" is almost immediately decolorised. "Aldehyde-green," on the contrary, becomes gradually blue, with appearance of three faint bands, of which the last lies in the extreme red, and can be recognised only by the aid of a very bright lamp-

light; the second is between *d* and C, and the third and weakest on D. The colours are easily extracted from the textures with alcohol, and can be determined in the solution by the prescribed reactions.

W. S.

Technical Chemistry.

Gas Lighting. By J. van Eyndhoven (*Dingl. polyt. J.*, **229**, 449).—It has been supposed that the gas flame is translucent. As, however, this appeared doubtful to the author, he determined to investigate the subject. The experiments were made with the aid of an excellent photometer, the results being as follows:—

The first experiments were made with a bat's-wing burner of 160 litres' gas consumption at 8·3 mm. pressure. The result of ten observations proved that the lighting power of the flat side was equal to 11·38, that of the narrow edge 10·04 candles. After correction for barometer and thermometer, the actual lighting power for normal consumption of gas and candle is 11·81 and 10·18 candles: English spermaceti candles with a normal consumption of 120 grains were used. For a flame consuming 100 l. of gas per hour, the actual illuminating power on the flat side was 9·03, on the narrow edge 7·42 candles, with a gas pressure of 4 mm. The difference in both cases is 1·5 candles, or 17 to 18 per cent., a circumstance which proves that the flame is not translucent, a bat's-wing burner giving most light on its flat side. An argand burner will from a similar cause not give all its illuminating power. For a good street illumination, therefore, the slits of the burners and the direction of the road must be placed perpendicularly on one another. D. B.

Some Peculiarities of the Vartry Water, and the Action of that Water on Boiler-plates. By C. R. C. Tichborne (*Chem. News*, **38**, 191).—The water of the River Vartry consists of organic matter of a peaty nature, and mineral matter, which consists chiefly of the chlorides of the alkalis and of the alkaline earths; nitrates and nitrites are also present, which, however, cannot be detected without evaporation, but as concentration by heat reduces the nitrates, the water was concentrated in a vacuum. This reduction, when it takes place in high pressure boilers, is a cause of the corrosion of the boiler plates. It was found that when iron was heated with nitrates in sealed glass tubes it became oxidised. E. W. P.

Preservation of Potable Water. By H. Schiff (*Deut. Chem. Ges. Ber.*, **11**, 1528—1529).—Water containing 3 parts of salicylic acid in 10,000 was found to be fresh after remaining in a flask for three years. Sea-water to which phenol or, preferably, carbon bisulphide (1 part to 1,000) has been added, forms a good preservative fluid for specimens of marine fauna. W. C. W.

Utilisation of Suint from Wool. By F. Fischer (*Dingl. polyt. J.*, **229**, 446—449).—It is known that raw wool contains about 20 per cent. of suint soluble in cold water, consisting of the potassium compounds of oleic, stearic, and acetic acids, a small amount of valeric acid, and many other organic substances, also of potassium chloride and sulphate, ammonium salts, and especially potassium carbonate, and sodium compounds.

By lixiviating wool with water, a dark brown liquid of peculiar smell is obtained, of sp. gr. 1·069; 1 litre of this required, for neutralisation, a quantity of normal acid corresponding with 3·98 grams of potassium carbonate. By neutralising 1 litre of liquor with hydrochloric acid and shaking up with benzene, only 916 milligrams of a yellow strongly smelling fat were obtained. By evaporating 1 litre and drying at 120°, 122·16 grams of a hygroscopic mass remained, which on ignition swelled up considerably, and evolved a gas burning with a bright flame. By continued heating in the air, and extracting with water and evaporating, 72·16 grams of a white saline mass, and 2·98 grams of a residue consisting of sand, alumina, lime, and phosphoric acid resulted. By burning the suint dried at 120° in a stream of oxygen, 3·04 per cent. of hydrogen as water and 19·92 per cent. of carbon as carbonic acid were obtained. The organic compounds of potassium are hereby converted into potassium carbonate.

A profitable recovery of the fat and the acetic acid is impossible, but the utilisation of the evaporated mass for gas and the production of potash can be recommended. For obtaining the potash present in the mass, the latter is in Germany merely heated strongly in reverberatory furnaces, the gas formed being used as fuel. Analyses of the composition of the flue gases showed that carbon monoxide is, in spite of the sooty nature of the flame, formed very rarely, and only when the mass is at its highest heat, in which case oxygen disappears. As soon as the evaporated liquors begin to burn, the heat evolved suffices to destroy all organic matter present. Thus with 1 kilo. of Westphalian coal 12 kilos. of liquors can be evaporated and ignited. The coke formed is solid. The following is the analysis of the coal dried at 120° :—

C.	H.	S.	O (and N).	Ash.
76·11	4·52	1·19	10·06	8·12

The raw potash taken from the furnace gave—

Salts soluble in water.	Insoluble.	Organic matter.
92·05	4·92	3·03

The composition of the soluble salts was as follows:—

K_2CO_3.	KCl.	K_2SO_4.	Na_2CO_3.
85·34	6·15	2·98	5·02 = 99·49 p. c.

W. Graff, in Lesum, works up this raw potash from six establishments for washing wool into pure potassium carbonate, bicarbonate, chloride, and sulphate. He employs about 10 to 12 workmen, the annual sale amounting to about 120,000 marks. D. B.

Analyses of Clays. (*Dingl. polyt. J.*, **229**, 451—455).—*Glaze-clay.*—As a very durable, perfectly impervious glaze on refractory clay, *e.g.*, for Bunzlau vessels, water pipes, &c., a very readily fusible clay is often used. Seger has analysed three specimens of these carthy glazes with the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alkalis.	CO_2.	H_2O and organic matter.
A.	58·99	11·73	4·16	4·77	1·83	4·83	16·19	4·80
B.	64·49	14·35	4·38	4·13	1·53	3·69	3·12	3·31
C.	62·40	15·51	5·68	4·36	1·13	3·62	2·88	4·41

A is one from Naumburg o. Q, used in Bunzlau for the manufacture of brown kitchen utensils and water pipes; B from Camenz i. S., used for the same purpose, and C is a glaze from the clay pipe manufactory in Dommitzsch o. Elbe.

The pyrometric investigations showed that, according to Seger's quotients of refractoriness (*ibid.*, **228**, 244), the Naumburg glaze was the most readily fusible, that of Dommitzsch the most difficultly fusible.

Stoneware-clay.—This clay, obtained from Höhr, and representing the raw material used for the manufacture of the fine, compact, pearl-grey vessels at that place, had the following composition:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O and Na_2O.	H_2O.
70·12	21·43	0·77	0·00	0·39	2·62	4·92

Wilkins has already pointed out the important influence which a large amount of silica in clay has on the lustre and the fineness of the salt-glaze; an observation which confirms the ready acceptation of the salt-glaze and the peculiar compactness of the above mass.

Porcelain Earth of Limoges.—These clays are not merely distinguished by the fineness of their forms, but the mass itself possesses a purer, more agreeable coloration, and greater fineness and strong transparency than the greater number of the German productions. The following is the composition of the kaolin:—

Ingredients.		Not decomposible	Decomposible	Clay substance decomposible by sulphuric acid.
		By sulphuric acid.		
SiO_2	58·39	32·22	26·17	47·09
Al_2O_3	27·52	7·49	20·03	36·04
Fe_2O_3	0·36	—	0·36	0·64
CaO	1·52	4·40	1·82	3·27
MgO	0·41			
K_2O	1·71			
Na_2O	2·58			
Loss by ignition	7·19	—	7·19	12·94
	99·68			

Corresponding with—

Clay substance	55·88
Quartz	5·95
Felspar	38·17

Compared with the composition of the German and Austrian kaolins (*ibid.*, **228**, 67), this substance is distinguished by an unusually high percentage of felspar, which explains also the fact that in Sèvres the mass is not mixed with felspar but merely with sand.

The porcelain from Limoges had the following composition:—

Ingredients.		Not decomposible (By sulphuric acid.)	Decomposible (By sulphuric acid.)	Composition of the clay substance.
SiO_2	66·71	47·27	19·44	45·35
Al_2O_3	21·58	5·93	15·65	36·50
Fe_2O_3	0·47	—	0·47	1·09
CaO	0·61	3·76	1·77	4·13
MgO	0·37			
K_2O	2·93			
Na_2O	1·62			
Loss by ignition	5·54	—	5·54	12·92
	99·83			

corresponding with clay substance = 43·04, quartz 26·46, and felspar 30·50.

The mass contains therefore more sodium, lime, and magnesia than, *e.g.*, the Berlin porcelain, a circumstance which explains its ready fusibility and greater transparency.

The glaze from Limoges consists of—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.
Ingredients in p. c.	74·99	14·80	0·37	1·09
Not decomposible by sulphuric acid	70·92	12·38	—	0·20
Decomposible by sulphuric acid	4·07	2·42	0·37	0·89

	MgO.	K_2O.	Na_2O.	Loss by ignition.
Ingredients in p. c.	0·36	4·31	3·49	0·65
Not decomposible by sulphuric acid	0·36		7·17	
Decomposible by sulphuric acid	—	0·68	—	0·60

Fürstenwald-glaze.—This glaze adheres in the form of sand to the lignite strata, and is used in the preparation of the lead and tin enamels for the fabrication of stoves. According to Seger, the mass dried at 120° has the following composition:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	K_2O.	H_2O and carbonaceous matter.
Total.....	85·96	7·30	2·22	0·25	1·97	2·12
Not decomposible by H_2SO_4	80·03	2·69	—	1·08		—
Decomposible clay substance.....	5·93	4·61	2·22	1·14		2·12

Eatable-clay.—Pattison Muir has investigated a clay-substance from Mackenzie County, in South Island, near New Zealand, which is eaten by men and sheep in large quantities. It has the following composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	NaCl.	H_2O.	Organic.
61·25	17·97	5·72	1·91	0·87	3·69	7·31	1·77

(according to R. Biedermann in *Notizb. d. Ver. für Fabr. von Ziegeln.* 1878, 229).

Grossalmerode-clay.—This clay is highly refractory and possesses great cementing power. It is coloured light bluish-grey to white, is shiny, and breaks up in water to a fine slimy mass. The following is the composition of the clay dried at 120°:—

	SiO_2.							
Al_2O_3.	Chemically combined.	Mechanically added.	MgO.	CaO.	Fe_2O_3.	K_2O.	S.	Loss by ignition.
34·52	43·38	6·53	0·73	0·76	1·66	1·51	0·26	11·04

This gives a chemical composition: $4·89(Al_2O_3, 1·65\ SiO_3) + RO$, and the quotient of refractoriness (according to Bischof) = 2·96.

D. B.

Blair's Process for Iron Manufacture. By J. Ireland (*Dingl. polyt. J.*, **229**, 458—461).—This paper gives a detailed account of the improvements which have been recently made in the working plant, also in the method of preparing iron sponge. A brief description of the reduction furnaces is given; these consist of a group of three vertical retorts, each retort having a diameter of 914 mm., and being 8·53 m. high. The furnace is surrounded by an outer casing of brickwork, leaving a combustion chamber between the inside of it and the outside of the retorts. The retorts were heated externally by gas jets, the air for combustion being supplied through apertures immediately above the gas jets. In 1876 Blair discovered, that by the addition of a small quantity of alkali to the carbonaceous matter mixed with the ore, the action of reduction was facilitated to a great extent, and ore which took about thirty hours to reduce without alkali, could be perfectly reduced in six hours with it. The existing furnaces, however, could not be altered in any way to suit the new condition of quickened reduction. Blair therefore abandoned the whole principle of heating, and adopted a system by which a stream of hot carbonic oxide was passed through the mass of ore and carbonaceous matter. The author, however, made use of the above furnace by dividing the cast-iron pipe inserted in the top of each retort into a number of smaller ones, so as

to present as small a column of materials to the action of heat as possible. He used a furnace of a height of 6·4 m., the retort being about 3·2 m. high, with four inserted tubes. A furnace of this description, 1·52 m. diameter and 12·92 m. high, produces from 60 to 70 tons of iron, and costs about 12,000 marks.

The cost of producing iron sponge will vary according to the locality in which the work is carried on, but with the furnaces introduced by Blair, the cost will be about 22 marks per ton, exclusive of the ore. Where several of the furnaces are in operation, the cost is less. Where the ore is rich and pure, iron sponge made from it can be at once made into tool steel, the quality of which cannot be equalled by that made from the best brands of Swedish bars. In the case of ore which is not so rich, the best way of utilising the sponge made from it is to melt it in a cupola furnace, transferring the molten mass to a Siemens-Martin furnace, wherein the mass is converted into steel. The pig metal obtained in this manner will contain about 1·5 per cent. carbon and 0·19 per cent. to 0·25 per cent. silicon.

D. B.

Phosphorus in Cleveland Ironstone and in Iron. By J. E. Stead (*Chem. News*, **38**, 14—18; 29—31 and 39—42).—This paper may be divided into six sections: (1.) The compound or compounds in which phosphoric acid exists in the Cleveland ironstone. (2.) Method of eliminating phosphoric acid from iron ores. (3.) The compound in which phosphorus exists in Cleveland metal. (4.) The effect, physically and chemically considered, which phosphorus has on pig metal. (5.) Method of removing it from pig iron. (6.) Phosphorus in bar iron. The following are the results of the analysis of the main Cleveland ironstone bed :—

	Stone analysed.	Iron.	Siliceous matter.	Phosphoric acid.	Moisture.	Loss by calcination.	Iron in the calcined stone.
	Main:	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
9 feet.	1st foot	26·53	18·30	1·46	8·50	27·39	36·50
	2nd ,,	29·54	10·90	1·13	9·10	29·80	42·08
	3rd ,,	29·14	10·68	1·13	9·50	29·80	41·50
	4th ,,	28·41	11·98	1·41	9·80	28·80	39·92
	5th ,,	29·97	9·00	1·17	10·00	30·83	43·31
	6th ,,	30·42	8·82	0·89	10·00	31·51	44·40
	7th ,,	29·70	9·00	0·80	10·10	31·78	43·53
	8th ,,	29·85	9·29	0·91	9·80	30·90	43·20
	9th ,,	30·30	12·01	1·16	9·00	28·50	42·40
	Black hard.						
21 ins.	7 inches	30·56	12·90	0·44	8·50	26·80	41·75
	7 ,,	27·87	22·20	1·12	5·50	18·00	34·00
	7 ,,	27·26	24·70	0·81	5·00	17·00	32·85

It will be seen from these analyses that no part of the stone is free from phosphoric acid. In the "Black Hard" bed, the author found this substance very variable in quantity, reaching as much as 3 per cent. in some cases, and only 0·25 per cent. in others.

1. As to the form in which phosphoric acid exists in Cleveland ironstone, the author mentions that several years ago Pattinson investigated this matter and concluded, judging from the non-action of ammonium sulphide on the stone, or rather on the compound containing phosphoric acid in the stone, that no iron phosphate was present, and that the phosphoric acid must be in combination with lime; and the results obtained by other methods of investigation employed by the author has confirmed this. It is the prevailing opinion that the source of all the phosphorus in the ironstone is the remains of small phosphatic animals; but this theory cannot be regarded as trustworthy, first, because in some parts of the "Black Hard" bed, where no fossil remains could be detected, the phosphoric acid has been found in large quantity, and secondly, because in all cases, on analysis, the shells and fossil remains which were taken out of the stone, were proved to contain much less phosphoric acid than the surrounding ironstone. The following analyses of fossil wood taken from various mines in that district will throw some light upon this very obscure subject.

Fossilised wood found in Cleveland ironstone—

OH_2.	C.	SiO_2.	CO_2.	SO_3.	S.	Mn.	Al_2O_3.
3·00	9·60	0·50	0·75	0·60	7·56	trace	8·25

CoO and NiO.	Co and Ni.	Fe.	FeO.	MgO.	P_2O_5.	CaO.
3·70	1·65	5·20	10·02	1·12	20·80	27·60

Several other samples gave similar results on analysis. There can be no doubt about the fact, that these samples were at one time parts of trees, which in their natural state would not contain more than very minute quantities of phosphoric acid. The latter must have been in solution, and has in this state passed into the substance of the wood and been there deposited in the condition in which we find it.

2. *Method of Removing Phosphoric Acid from Ores.*—Jacob's method, based on the treatment of the ores with sulphurous acid produced by burning sulphur pyrites and condensing the acid fumes in coke towers, gave satisfactory results only when the stone was reduced to a very fine powder, about 90 per cent. of phosphoric acid being removed thereby. Forbes' method, based on the action of common salt on iron phosphate when fused, also gave unsatisfactory results, as did the last method referred to by the author, the action of sodium carbonate on phosphate of lime when fused with it. From this it would seem that Cleveland ironstone cannot be freed from phosphorus by any methods as yet proposed. With regard to the smelting of ironstone, since we know that phosphate of lime heated with carbon and iron oxides, or metallic iron, to a very high temperature, is decomposed, the phosphorus combining with the iron, it is to be expected that nearly all of the phosphorus introduced in the charge at the top of the blast-furnace, will be found concentrated in the pig metal. Experiments showed that fluorspar is of no value in removing the phosphoric acid or preventing its passage into the metal when employed as a flux in smelting.

Iron and Phosphorus.—By direct addition of phosphorus to iron heated in a crucible, the author obtained combinations containing between 6 and

27 per cent. of phosphorus, although Percy has stated that iron will not take up more than 8·4 per cent. of phosphorus when the two substances are heated together in the manner described. The fusion point appears to decrease with each addition of phosphorus, until a compound containing from 10 to 12 per cent. of phosphorus is produced, which is the most fusible; after which each addition makes the compound less and less fusible.

3. *The Compounds in which Phosphorus exists in Cleveland Metal.*—Judging from the comparative fusibility of iron, it was thought that if separate compounds of iron and phosphorus existed in pig metal, these compounds would be more fusible than the bulk. Analyses of about 1 cwt. of Cleveland iron poured into a mould were made. After the mass had become viscous, extreme pressure was applied by means of a hydraulic ram, and the portions of metal last fluid expressed. The expressed metal was found to be a combination of phosphide of iron and unaltered pig metal in the proportion of 51·5 : 48·5 or 88·05 per cent. of iron and 11·95 per cent. of phosphorus; or, calculated into chemical equivalents, they are in the ratio 1·57 iron to 0·385 phosphorus or 4 equivalents of iron to 1 of phosphorus, and the formula may therefore be written Fe_4P. It is very clear from these results that phosphide of iron does exist in a separate state in pig metal intimately diffused throughout the mass. On immersing bar iron in dilute acid, such as hydrochloric acid or sulphuric acid, a black residue is observed adhering to the outside of the iron. In these residues, phosphides of different constitution were found, the iron and phosphorus being present as Fe_3P_4 and Fe_3P_2. This fact proves that iron containing phosphorus contains two or more different phosphides, and that they exist in very varying proportions in different samples of iron.

4. *The Effect which Phosphorus has on Pig metal* (*a*). *Physical Properties.*—Experiments have shown that, as a considerable quantity of iron is in combination with phosphorus in Cleveland iron, there is less iron remaining capable of taking up silicon, than is the case where no phosphorus is present: consequently less silicon will be required to give to the smaller proportion of iron the conditions necessary for the production of glazed iron. (*b.*) *Chemical Properties.*—When sulphur is added to fluid metal—which under ordinary circumstances would assume a grey fracture when cooled and broken—the sulphurised iron when cold will present a mottled or white fracture. In other words, sulphur prevents the separation of carbon as graphite. In order to ascertain if phosphorus has a similar action, experiments were made which proved that the effect of phosphorus compared with that of sulphur is very small, and would not affect materially the quality of the iron or pig in this direction, even if increased in considerable quantity.

5. *Methods of removing Phosphorus from Pig metal.*—The action of oxide of iron as a purification method is well known, but it has frequently been supposed that oxide of iron, without the aid of mechanical power, has very little action, and that the work a puddler gives to the metal has some important action in removing phosphorus independent of the oxide of iron. By the results obtained from numerous experiments it has been clearly proved that mechanical power, whether it

be in the force of the refining blast, the motion of the puddler's bar, or the revolving of the rotary puddling machine, is simply the means by which the molten iron is brought into intimate contact with the fluid or semi-fluid oxide of iron. The removal of phosphorus depends entirely on this, and not on any mechanical force. It is further illustrated experimentally that, when the puddling process is conducted at a very low temperature, or when the cinder is run out of the furnace before the phosphorus is removed, the puddled bar produced is high in phosphorus. In the first case the temperature is not high enough to liquefy the necessary amount of cinder required for the purification of the metal, and as a consequence, there is left an impure iron; whilst in the other, when the cinder is removed from the semi-purified iron the purifying agent being taken away, the removal of phosphorus is retarded and a phosphuretted iron is produced. On the other hand, when a high temperature is maintained, a very excellent quality of bar is produced.

6. *Iron Heated with Phosphoric Acid.*—It is stated that pure iron at a red heat has no power to decompose phosphoric acid; but, if the iron be heated to its fusion point, the acid is readily decomposed. Pure iron was fused with puddler's tap-cinder, containing above 4 per cent. of phosphoric acid, in order to determine whether or not pure iron would decompose phosphoric acid when in combination with iron oxide: the button produced contained = 2·12 per cent. Pure iron was next fused with phosphate of iron, and the metal, after fusion, was found to contain 2·68 per cent. of phosphorus. The nature of the action between oxide and phosphide of iron was proved by experiments to be not physical but chemical. The button obtained weighed about 15 per cent. more than before such treatment.

6. *Phosphorus in Bar-iron.*—From the following results it will be seen that a considerable amount of phosphorus is removed by simply heating and rolling iron containing it; and that it is oxidised and removed from the iron, whereby the quality of the bar is improved considerably. No. 2 ordinary bar-iron made from Cleveland pig was twice piled and rolled. No. 4 bar, produced after the second rolling, was excellent fibrous iron, and very soft, whereas, before the treatment, it was in great part crystalline and hard:—

	Phosphorus combined with iron. p. c.	Phosphorus in cinder. p. c.	Phosphorus. Total. p. c.
2.	0·243	0·087	0·33
3.	0·130	0·110	0·24
4.	0·071	0·149	0·22

The following is an analysis of three finished bars made from Cleveland iron, puddled in the Danks' furnaces at the Tees Side Iron Works. It would be difficult to obtain better iron than this:—

	I. p. c.	II. p. c.	III. p. c.
Carbon	0·080	0·110	0·160
Silicon	0·092	0·046	0·040
Sulphur.....	0·012	0·016	0·012
Phosphorus	0·110	0·060	0·073

	Phosphorus combined with iron.	Phosphorus in cinder.	Phosphorus. Total.
	p. c.	p. c.	p. c.
1.	0·057	0·063	0·110
2.	0·023	0·037	0·069
3.	0·034	0·039	0·073

In the third portion of his paper the author describes some of the changes which take place when air is blown through phosphuretted metal, and considers the value of manganese oxides, chlorine, bromine, iodine, and hydrogen as agents for removing phosphorus, leaving the question of ore purification as a yet unsolved problem, and one which will not be readily solved to the satisfaction of the practical iron manufacturer.

When metal containing manganese, silicon, carbon, and phosphorus is acted upon while in the fluid state by a stream of air, there is every reason to believe that all the elements present, probably with the exception of carbon, are oxidised in the ratio in which they exist in the metal, and this should give a very basic cinder. Such, however, is not the case: for almost instantly after the formation of cinder, the manganese, silicon, and phosphorus still present in the fluid mass are oxidised by the oxygen of the protoxide of iron, while the reduced iron, leaving the cinder, returns to the bath and is replaced by the oxide of manganese, silicon, and phosphorus. In consequence of the rapidity with which these reactions take place, the cinder drawn off from the metal is always more or less saturated with silica, phosphoric acid, and manganese oxide. In a Bessemer converter, when the temperature is low enough, there can be no doubt that at first all ingredients are burnt just in the proportion in which they are present. Such, however, is the violent agitation to which the metal is subjected, that the cinder and iron are continually in intimate contact, and as a consequence, the cinder is very rapidly saturated with silica and phosphoric acid. In the Bessemer converter, after the saturation point has been reached, when the silica and phosphoric acid have both in combination with them the proper chemical proportion of oxide of iron, the still unoxidised silicon in the metal will continue to reduce the oxide in the cinder, and will replace it by silica. It is clear that when this point has been attained, viz., the removal of a base and the substitution of an acid in a compound already saturated with acid (silica), silica must be in excess, and that, as this acid is much more powerful than phosphoric acid, it will take away the oxide of iron at first in combination with it, by which reaction silicic acid and iron phosphates are transformed into phosphoric acid and iron silicate. Experiments were undertaken which afforded proof of the theory, that manganese is capable of reducing free phosphoric acid at a comparatively low temperature. It was further shown that the attraction of silicon for oxygen is greater than the attraction of phosphorus for that element, and that when free phosphoric acid is exposed to the action of silicon, as it exists in fluid metal at low temperatures, oxygen is withdrawn from the phosphoric acid, and combines with the silicon to form silicic acid. The results of an experiment in which fluid iron containing little or no silicon or manganese, was poured

upon solid phosphoric acid placed at the bottom of a red-hot crucible, clearly showed that the acid had suffered decomposition.

As the question as to the point at which oxide of iron becomes saturated with silica is very important, several experiments were made with the view of solving it. For this purpose cinder containing little more than a trace of phosphoric acid was mixed with variable proportions of sand, and, after fusion, was agitated with fluid iron containing phosphorus. In each case the metal was tested for phosphorus after treatment, and if no diminution was detected, it was concluded that the cinder employed contained no free iron oxide. The results were as follows:—

	No. 1. p. c.	No. 2. p. c.	No. 3. p. c.	No. 4. p. c.
Protoxide of iron	73·90	64·50	55·50	47·68
Sesquioxide of iron	11·60	10·60	8·50	6·87
Silica	10·50	20·40	31·00	40·00
Alumina, lime, &c.	4·00	4·50	5·00	5·45
	100·00	100·00	100·00	100·00

	No. 5. p. c.	No. 6. p. c.	No. 7. p. c.	No. 8. p. c.
Protoxide of iron	42·13	43·41	38·57	29·57
Sesquioxide of iron	10·71	8·13	7·86	5·00
Silica	44·00	46·00	51·00	62·50
Alumina, lime, &c.	3·16	2·46	2·57	2·93
	100·00	100·00	100·00	100·00
Metallic iron	65·60	57·60	49·12	41·89
Ratio of iron to silica	1 to 0·16	0·35	0·63	0·95
Phosphorus in metal—				
Before treatment	1·51	1·51	1·48	1·48
After treatment	0·13	0·04	0·25	0·75
Metallic iron	40·27	38·34	38·50	26·50
Ratio of iron to silica	1 to 1·06	1·20	1·44	2·36
Phosphorus in metal—				
Before treatment	0·91	0·91	0·91	0·91
After treatment	0·89	0·90	0·91	0·91

It will be seen that when the ratio of iron to silica in the cinder is as 1 to 1·06, the compound is incapable of oxidising phosphorus from fluid iron containing it. This ratio is almost exactly the same as that of the chemical equivalents of iron and silica, viz., as 56 to 60. It will be noticed that there has not been so much phosphorus removed in No. 1 as in No. 2, in which the cinder was not so pure as in the first case. This, however, was due to the very sluggish nature of the cinder, which prevented its intimate admixture with the metal.

It was proved by experiment that, within certain limits of temperature, it is impossible to drive off from cinder its phosphoric acid by

the addition of silica. The analysis of the cinder made after fusion showed that it tenaciously retains phosphoric acid, confirming the theory that the whole of the phosphorus removed in the various processes in which oxide of iron is used for purifying iron, is contained in the cinder, and that none is vaporised and carried up the stack with the waste products of combustion from the furnace grate.

As to the value of manganese oxides as agents for purifying iron from phosphorus, it is mentioned that the protoxide, retaining its oxygen with much greater tenacity than the sesquioxide, and being decomposed at very high temperatures only, in presence of reducing agents, is without any direct action on the phosphorus existing in the fluid iron; as, however, this oxide has a much greater attraction for silica than iron oxide, it plays a part of secondary importance in the cinders of the purifying processes by taking up the silica. By forcing peroxide of manganese under the surface of molten iron, it is deprived of half its oxygen, which, acting upon the oxidisable impurities in the metal, removes them. When oxide of iron acts upon phosphorus, for each part of that element oxidised, 4·5 parts of pure iron are removed from the oxide. When manganese peroxide acts upon phosphorus the oxidation is effected by free oxygen, and therefore there is no gain by the separation of metal. It would seem, therefore, that peroxide of manganese is of much less value than iron oxides. With regard to the value of fluorspar as an agent for removing phosphorus, the following experiment was tried. The action of a mixture of fluid oxide of iron and fluorspar upon Cleveland iron was ascertained by fusing two-thirds of mill-tap and one-third of spar, and thoroughly well mixing up with molten iron, the result being the removal of the greater part of the phosphorus. As to the use of chlorine, bromine, and iodine, it is mentioned that since all these elements form definite compounds with phosphorus, which are all decomposed when brought into contact with red-hot iron, the phosphorus combining with the iron, there would be no advantage derived from their use. Hydrogen also is incapable of removing phosphorus from iron, as iron will withdraw phosphorus from its combination with hydrogen. Water has been advocated as an agent for removing phosphorus, it being held that the hydrogen would combine with it and pass off as phosphoretted hydrogen. An experiment was undertaken with the following results:—

Pig metal.	Before.	After.
Phosphorus.....	1·48 p. c.	1·48 p. c.

Analysis of gases evolved from molten Cleveland iron in water:—

H.	CO.	CH_4.	H_2S.	CO_2.	P_2O_5.	p. c.
79·69	12·48	4·87	1·74	1·22	None	= 100

The metal lost half its sulphur by the operation.

In concluding this paper the author remarks, that so far as our present knowledge goes, there is nothing to surpass, in point of cost and efficiency, the process of purifying by means of oxide of iron.

D. B.

Manufacture of a Red Pigment from Iron Scrap. By R. and C. Steinau (*Chem. Centr.*, 1878, 336).—This pigment is formed by exposing wrought-iron shearings to the alternate action of air and water, and heating the resulting hydrated oxide to redness with access of air. Black is obtained by using reducing agents, and brown by mixing the two pigments. J. M. T.

Preparation of Rosemary-oil. By C. O. Cech (*Dingl. polyt. J.*, **229**, 466).—In the island Lesina, the rosemary plant attains a height of 30 to 62 cm., and, where it is carefully cultivated, 125 cm., the stems having a diameter of 2 to 3 cm. The glands filled with the ethereal oil (*Oleum rosmarini*) are situated on the under side of the leaves. The manufacture of this oil in Lesina is increasing daily. Although no positive data exist as to the production of this oil, it is nevertheless known that Lesina ten years ago sent out 30,000 fl. Austr. worth of it.

Every third year the biennial sprouts of the rosemary shrub are clipt in the month of May, the branches being dried for a week in the sun, and then deprived of their leaves. The distillation of the oil is made in copper stills, placed close by the sea shore, and heated over an open fire. Before charging the still, the dried leaves are moistened with water. The oil volatilising with the vapours of water passes through a worm and is collected in bottles. After separating the water from the oil, the latter is filled into tin vessels and sent to Trieste. Rosemary-oil is mostly used in perfumery, but is also added in small quantity to olive-oil; the latter suffers no loss in value for technical purposes by this treatment, whilst the high duty imposed on olive-oil is avoided. From Trieste 17,000 to 20,000 kilos. of rosemary-oil are annually brought into commerce at an average price of 2 fl. per kilo. In France and Spain an alcoholic extract has for some time been prepared from this oil and other perfumes, which was known under the name of *aqua reginae Hungariae*. This preparation had its origin in Lesina.

Besides rosemary-oil, the dried leaves of this plant are sent into commerce as spices, and for use in the smoking of meat, and for the preparation of rosemary-wine and rosemary-vinegar. D. B.

Inactive Glucose in Crude Cane-sugars. By U. Gayon (*Compt. rend.*, **87**, 407).—The optically inactive glucose contained in crude cane-sugar and in molasses has been supposed to consist of a mixture of dextroglucose and levoglucose in due proportions. The paper describes experiments which confirm this opinion, and exhibit a means of transforming, by fermentation induced by pure *Mucor circinelloïdes*, the glucose of molasses into alcohol, and consequently of extracting additional quantities of crystallisable sugar from it.

R. R.

Analyses of Lamp-black made from the Natural Hydrocarbon Gas of the Ohio Petroleum Region. By J. R. Santos (*Chem. News*, **38**, 94).—There are two wells in Knox County, Ohio, near the junction of the Kokosing and Mohican rivers, yielding very large quantities of hydrocarbon gas, which Neff, of Gambier, has

utilised in the manufacture of a lamp-black, which he calls "diamond black." In the building used, 1,800 burners are at work, consuming about 275,000 cubic feet of gas per 24 hours, being about one-fourth of the available supply. The following is the composition of the gas by volume:—

CH_4.	C_2H_6.	N.	O.	CO.	CO_2.	
81·4	12·2	4·8	0·8	0·5	0·3	= 100·0

Hydrogen, although not mentioned, is, according to Sadtler, present in small quantity. The lamp-black is at present manufactured to the extent of about 16 tons per annum. It is very fine and smooth, free from coarse or gritty particles, and of a deep blue colour. It is sold to makers of fine printing and lithographic ink in the United States. The following analysis was made:—Sp. gr. at 17° after complete expulsion of air, equals 1·729. The air-dried lamp-black lost by exposure at ordinary temperature over sulphuric acid 2·30 per cent. of moisture, and a further loss of 0·40 per cent. was experienced by heating to 100°. Continued heating at 200° and then at 300° under atmospheric pressure gave rise to no further loss, but a minute amount of water was expelled by subsequently heating in a Sprengel vacuum. The material dried at 200° gave in two combustions:—

I.	Carbon....	96·041	Hydrogen....	0·736	
II.	„	96·011	„	0·747	

The occluded gases, driven out by heating to low redness in a Sprengel vacuum, represented, on calculating weight from volume:—

CO.	CO_2.	N.	Vapour of water.
1·378	1·386	0·776	0·682 p.c. by weight.

There was also expelled and condensed on the cooler part of the tube 0·024 of a solid light-yellow hydrocarbon, soluble in alcohol, fusible, and volatilising rapidly under atmospheric pressure between 215° and 220° (impure naphthalene ?).

Hence the composition of the lamp-black may be calculated as—

C.	H.	N.	CO.	CO_2.	H_2O.	Ash (F_2O_3 + CuO).	
95·057*	0·665*	0·776	1·378†	1·386†	0·682	0·056	= 100·000.

D. B.

The Part played by Coal-dust in producing Explosions in Coal Mines. By L. Simonin (*Compt. rend.*, **87**, 195—197).—Explosions have been known to occur in coal mines which were free from explosive gases, and this is attributed to the presence in the galleries of the mine of finely-divided coal-dust, which, in the event of a very slight explosion of fire-damp or of powder when blasting the coal, rapidly disengages its coal-gas and increases the force of the explosion. A. J. C.

* Including the C and H of 0·024 solid hydrocarbon.

† These gases were doubtless partly formed from solid carbon and occluded oxygen by the heat applied in the vacuum.

Abnormal Solubility of certain Bodies in Soaps and Alkaline Resinates. By A. Livache (*Compt. rend.*, **88**, 249).—The soaps known in commerce as "petroleum soaps" are made by adding to ordinary soap petroleum mixed with a certain proportion of Carnauba wax. On heating the soap, the petroleum easily distils out, leaving the soap unaltered; these soaps are entirely soluble in water. This latter property is due to the Carnauba wax which they contain, or rather to the melissic alcohol contained in that body, for petroleum alone is quite insoluble in soap solution, but dissolves in melissic alcohol. Other bodies, such as wood-spirit, amyl alcohol, &c., act in like manner, very small quantities of these solvents sufficing to dissolve as much as 50 per cent. of petroleum in soap. Turpentine oil and other liquids, suspended in soap-solution, dissolve on addition of coal-tar oil dissolved in the same solution. C. W. W.

Kallab's New Bleaching Process for Animal Textile Fibres. (*Dingl. polyt. J.*, **229**, 89—92).—The following method has been used with success by the author for bleaching silk, and more especially wool with the use of indigo and Schützenberger's hyposulphurous acid, H_2SO_2 (*Dingl.*, **225**, 383). The material to be bleached is cleaned in the usual manner (*Dingl.*, **225**, 389) and brought in its moist state into a bath of clean water at the ordinary temperature, to every 100 litre of which 0·5 to 1 gram of finely-powdered reddish-blue indigo has been added. After a short treatment in this bath, the material is taken out, pressed, and taken to the bleaching bath. The latter consists of a solution of freshly-prepared sodium hyposulphite of 1·0069 to 1·0283 sp. gr.; to each litre of liquid 5 to 20 c.c. of 50 per cent. acetic acid are added. The latter must be free from strong mineral acids. The operation is conducted in closed vessels. The mechanically adhering indigo is reduced to indigo-white, and taken up in a dissolved state by the fibre, whilst the sulphurous acid given off simultaneously bleaches the latter. After 6 to 24 hours' exposure in the bath, a sample is taken out. If the latter is quite white and shows a slight bluish tinge, the operation is finished; the whole is taken out of the bath, allowed to drain, and finally exposed to the air. The indigo-white is reconverted into indigo blue, producing a perfectly fast azurage of the fibre. If concentrated bleaching baths are used, a subsequent treatment with 0·5 to 1 per cent. solution of crystallised soda may be recommended. Loose wool may be bleached in a more concentrated bath of 1·0356 to 1·0431 sp. gr., without the addition of acetic acid. For yellow shades, it is preferable to use calcium hyposulphite instead of the sodium salt, a bath of 1 to 1·0283 sp. gr. being the most suitable. In this case the previous treatment with indigo is unnecessary. If the white shows a greenish tinge, the stuff is drawn through a water-bath acidulated with hydrochloric or sulphuric acid. For silk, the bleaching liquid must be much weaker than for wool. This process may also be employed for bleaching feathers, bathing sponges, lines, hemp, cotton, wood, and straw.

D. B.

Advantages of only Partially Removing the Fat in Oil-Seeds. By L. Wittmack (*Dingl. polyt. J.*, **229**, 167).—When some

time ago the idea originated of extracting the fat from oil-seeds by means of carbon bisulphide instead of by pressure, it was generally feared that the residue could not be used as fodder, because at that time no satisfactory method had been found of completely removing the carbon bisulphide. Since it has been found possible in practice to completely remove the carbon bisulphide from the residue, the latter has been largely used as fodder, with advantage both as to the yield of milk and also with regard to the breeding and fattening of animals. It was, however, regretted by farmers that during the last decade the extraction of fat had become so perfect, that the residue was poor in fat compared with that obtained by pressing. It nevertheless remains to be proved whether for fattening purposes an increased quantity of fat is needed, the mast itself being very nourishing. Trials made by Wolff, Funke, and Kreuzhage in this direction gave no material difference, although it is stated that an increase in the quantity of fat undoubtedly has a more nutritious action, especially with regard to the fattening of animals, from the increased utilisation of the whole fodder in the formation of fat and flesh. For this reason manufacturers have given up the idea of completely extracting the fat from oil-seed. Moreover, by extracting merely a large proportion of the fat, they are able to operate on a much larger quantity of seeds with the same plant. D. B.

On Tanning and Mineral Tanning. By Gottfriedsen (*Dingl. polyt. J.*, **229**, 180—182).—The editor of the *Halle aux Cuirs* in Paris obtained some time ago samples of iron-tanned leather (Knapp's patent, *Dingl.*, **227**, 86 and 185) from Gottfriedsen, of Braunschweig; these were forwarded to Müntz, who, after examining them, published his results in that Journal (January 10). He considers that real leather always consists of a chemical combination of the tissues of the skin with tannin, every mechanical or physical union being merely a false leather without real value for application. He therefore subjected iron-tanned leather to a treatment with sulphuric acid, and concludes from the results obtained, that the ferric oxide is not present in a combined form, and, moreover, that iron-tanned leather is not leather at all, but is perfectly useless as such. According to his views, the oxide in iron-tanned upper leather is merely a solution of ferric oxide in fat. However, by comparing mineral tanned leather with ordinary leather (tanned leather), he does not go further than the "evident proof" that the latter is a chemical combination, without giving any explanation as to what this evidence is. The authors, therefore, undertook to complete this investigation. They found that leather made with vegetable tannin was more easily decomposable than iron-tanned leather. The same was the case with tanned or chamois leather. D. B.

General and Physical Chemistry.

Influence of Temperature and Pressure on the Spectra of Gases. By G. Ciamician (*Chem. Centr.*, 1878, 689).—The spectra of chlorine, bromine, and iodine in the gaseous state show considerable differences. Diluted bromine vapour gives a spectrum analogous to that of chlorine; when examined under pressure, the bromine spectrum approaches that of iodine. The spectrum of iodine vapour under considerable pressure is not comparable with that of any of the other halogens under any circumstances; so also dilute chlorine yields a spectrum presenting little analogy to those of bromine and iodine, whilst the spectrum of compressed chlorine is closely analogous to that of diluted bromine or iodine.

The spectra of those elements, which exhibit great chemical activity (H, Na, O, Cl, Br, I), are markedly altered by increase of pressure.

M. M. P. M.

Spectroscopic Investigation of the Constitution of Liquids. By H. Burger (*Deut. Chem. Ges. Ber.*, **11**, 1876—1878).—The author describes an apparatus he has constructed for the investigation of the questions—(1.) Are the absorption-bands of mutually indifferent liquids affected by mixture? (2.) Is the absorption-spectrum of a liquid affected by its temperature? He is engaged in investigating solutions of Co, Cu, and Na salts.

C. F. C.

Absorption-Spectra. By J. Landauer (*Deut. Chem. Ges. Ber.*, **11**, 1772—1775.—On the addition of a concentrated acid to a safranine salt, the red colour of its solution changes to violet, indigo-blue, and finally to emerald-green. The change of colour takes place in the reverse order, when water is added to the acid solution of safranine. The solution gives a characteristic spectrum for each colour.

In a compound of picric acid with safranine or with rosaniline, picric acid can no longer be detected by means of the spectroscope. From these facts, the author concludes that absorption-spectra can provide a clue to the composition of a compound only when the colour of the substance is characteristic of its chemical composition.

W. C. W.

Planté's Secondary Battery. By R. Böttger (*Chem. Centr.*, 1878, 574).—According to Planté, if two spirals of thin sheet lead immersed in dilute sulphuric acid are connected with the wires from a battery, the anode spiral becomes covered with lead peroxide, and the cathode with a grey compact film. If the battery be disconnected when oxygen begins to be evolved at the anode, the lead spirals are said to act as a powerful battery, and to retain their electromotive force for some days. The author finds, however, that the electromotive force diminishes rapidly, and that after 24 hours no further action is obtainable from such an arrangement.

M. M. P. M.

Production of Rotatory Movements in Mercury. By R. Böttger (*Chem. Centr.*, 1878, 560).—If a drop of pure mercury, 3 or 4 mm. in diameter, placed on a watch-glass, and covered with a dilute solution of mercuric nitrate, be touched with a rod of zinc about the size of a needle, a peculiar palpitating movement of the drop becomes visible; if a second rod of zinc be now brought into contact with the mercury, the drop rotates rapidly; after a time the motion ceases. The action is no doubt caused by electric currents.

M. M. P. M.

Production of a High Temperature by means of Ammonium Nitrate. By R. Böttger (*Chem. Centr.*, 1878, 560).—If ammonium nitrate be dissolved in water, the temperature falls considerably, but if zinc-dust equal in amount to the ammonium nitrate used be now thrown into the liquid, the temperature suddenly rises, and the liquid boils violently; if the experiment is performed in a beaker or a flask, the vessel is generally shattered. M. M. P. M.

Material for Standard Weights and Measures. By F. Mohr (*Ann. Chem.*, **194**, 40—53).—On looking over tables of co-efficients of expansions, it is found that for 1°, platinum expands 9-millionths of its length; iron, 11; glass, 9; Carrara marble, 8; black marble, $4\frac{1}{2}$. The last-named material, the uncrystallised black marble, has been already used with success for the stems of pendulums. It is recommended now that this substance be used for constructing an unalterable standard measure. The material is to be had suitable for any dimensions, is easy to work, takes a beautiful polish, and is soft enough to yield readily to the diamond for the graduation of an entire meter. For weights, rock crystal is recommended. It is of importance that all weights should be made of a material of the same density, so that displacement and alteration through atmospheric conditions shall be the same in every piece. It is also important that the specific gravity of the pieces shall approximate as closely as possible to that possessed by most of the bodies separated out in analysis, and again that they have a considerable degree of hardness to protect them against wear and tear. Instead of rock crystal, the author proposes massive glass containing a large proportion of silica. For the smaller weights he recommends aluminium (specific gravity = 2·56), instead of platinum, or perhaps a somewhat heavier and more durable alloy with silver. All pieces to be round, and to be taken hold of in the middle, not at the edges. Except in gasometric operations, it has so far never been thought necessary to take into account the conditions indicated by thermometer and barometer on weighing.* The influence and effect of different elevations above the sea level, with weights some of brass and some of platinum in the same set, is not noticed. A kilogram weight of rock crystal on one day, by a barometric fall of 10 mm. on the next may be reduced by 5·3 mgms. Why, then, adjust a standard kilogram to the decimal of a milligram, if atmospheric

* *Abstractor's Note.*—At any rate an exception to this assertion may be mentioned in the case of Crookes's determination of the atomic weight of thallium, where the influence of barometic pressure was taken into account.

changes indicated by barometer and thermometer can produce such an effect? In the original derivation of the kilogram, three practical errors were made: (1.) That water of 4° was chosen as object of comparison. Water of any other temperature has just as definite a volume at that temperature as at 4°, and the latter is not to be had in the greatest part of the year, and not only the water, but also balance and weight, and the whole surroundings generally, must possess the same temperature, if a weighing lasting some considerable time is to be of value. On the contrary, it is easy to keep to a mean temperature of 17·5° for any length of time. (2.) That the weighing should have been made *in vacuo*. That this could not have been correctly done arises from the facts that the weight of a litre of dry air of normal constants was not known, and finally, because the third error was committed. (3.) That the specific gravity of the platinum employed had not been estimated. It is unknown if the temperature of the air and objects and barometric pressure were noted in the comparison. With regard to the new standard measure, it is in the highest degree indifferent what fraction of the earth's circumference it makes.

W. S.

Inorganic Chemistry.

Formation of Hydrogen Peroxide by the Explosion of a Mixture of Oxygen and Hydrogen. By R. Böttger (*Chem. Centr.*, 1878, 574).—If two volumes of hydrogen and one volume of oxygen be exploded in a small flask, hydrogen peroxide may be readily detected after the explosion, by adding a little starch-paste containing cadmium iodide in solution, followed by the addition of a crystal of ammonium-ferrous sulphate.

By exploding ether vapour mixed with air, ozone is produced, but no peroxide of hydrogen; a similar experiment with anhydrous alcohol yielded no ozone. M. M. P. M.

Reduction of Iodates by Phosphorus. By J. Corne (*J. Pharm. Chim.*, [4], **28**, 386—389).—Moist phosphorus in presence of air, reduces iodic acid and iodates at the ordinary temperature, but if air be excluded no reduction takes place. This reduction cannot be due to phosphorous or hypophosphorous acid, because in the case of the former, reduction only takes place at a temperature of 80—90°, and in the latter at about 50°.

If phosphorus is immersed in water, and the air above the water confined, the phosphorus becomes oxidised, and the products of oxidation are dissolved in the water. This solution will immediately reduce potassium iodate. The author, therefore, supposes that besides phosphorous and hypophosphorous acids being formed, a body more greedy for oxygen than the latter, perhaps an acid containing less oxygen, is

formed, and that hypophosphorous acid, H_3PO_2, is the second of a series of acids, in which this unknown body stands first, with a formula, H_3PO. Mercury often prevents this reduction.

L. T. O'S.

Solubility of Sulphur and Phosphorus. By G. Vulpius (*Arch. Pharm.* [3], **13**, 229—231).—At 100°, 1 part of sulphur is soluble in 2,800 parts of strong formic acid, but is separated from its solution on cooling; the separation is less remarked if the solution is diluted with water of the same temperature, but it is very evident if the water is cold. The contrary takes place in the case of a solution of phosphorus in acetic acid, the precipitation being greater if the liquid be diluted than if it be cooled. Phosphorus is soluble in formic acid only in traces. Of all the fatty acids, stearic acid is the only one which dissolves any appreciable quantity of phosphorus or sulphur. An alcoholic solution of the stearic acid solution of phosphorus when cooled, assumes a gelatinous form. E. W. P.

Researches on the Sulphates. By A. Etard (*Compt. rend.*, **87**, 602—604).—The new compound sesquisulphates previously described by the author are not the only combinations possible. Bodies of the general form, $M_2(SO_4)_3.NSO_4.nSO_4H_2$; compound sulphates of the formula $2(SO_4MSO_4N).nSO_4H_2$; and simple or double more or less hydrated sulphates may be obtained.

Ferrosoferric Sulphate, $Fe_2(SO_4)_3.FeSO_4.2H_2SO_4$ is obtained in small, pink, hexagonal plates, by dissolving in as little water as possible equivalent quantities of ferrous and ferric sulphates, adding a great excess of concentrated sulphuric acid, and heating to about 200°. In a similar way have been also prepared, $Cr_2(SO_4)_3.NiSO_4.2SO_4H_2.3H_2O$, $Cr_2(SO_4)_32SO_4Fe.SO_4H_2.2H_2O$, $Cr_2(SO_4)_32SO_4CuSO_4H_2$, $Fe_3(SO_4)_3.SO_4Ni.2SO_4H_2$, $Fe_2(SO_4)_3.2SO_4Mn.3SO_4H_2$, $Al_2(SO_4)_3.2SO_4Fe.SO_4H_2$, $Al_2(SO_4)_3.2NiSO_4.SO_4H_2$.

All these salts are insoluble in water, but are decomposed by it after a time. The above formulæ, together with the author's other observations, show that a molecule of acid can replace a molecule of protosulphate in these compounds, and *vice versâ*, according to the nature of the metal and the temperature.

The compound protosulphates are prepared by dissolving the corresponding salts in as little water as possible, and precipitating by a large excess of concentrated sulphuric acid. Thus are obtained $2(NiSO_4ZnSO_4)SO_4H_2$, $2(FeSO_4ZnSO_4)SO_4H_2$, $2(CuSO_4ZnSO_4)SO_4H_2$, $2(CuSO_4CoSO_4)SO_4H_2$, $2(FeSO_4CoSO_4)SO_4H_2$, $2(SO_4CuNiSO_4)SO_4H_2$, and $2(NiSO_4FeSO_4)2SO_4H_2$. With the ferrous and cupric sulphates, a brick-red crystallised salt is precipitated. This contains $SO_4CuSO_4Fe.2H_2O$; it loses its water at a higher temperature, turns violet, and then contains $SO_4Fe.SO_4Cu$, keeping its crystalline form. These salts are not oxidised by fuming nitric acid, even on boiling. $SO_4Cu.SO_4Mn.H_2O$ and $SO_4Cu.SO_4Ni.3H_2O$ are also obtained in microscopic crystals by the same method.

By substituting the simple salts for the preceding mixtures, the mono- and bi-hydrated salts are obtained in crystalline form:—

$SO_4Co.H_2O$, $SO_4Ni.2H_2O$, SO_4ZnH_2O, SO_4CuH_2O, SO_4FeH_2O.

The protosulphates dissolved in boiling concentrated sulphuric acid are deposited in crystalline form. All these bodies present to the naked eye a more or less shining sandy appearance. The nickel and cobalt salts are gradually decomposed and dissolved by water.

C. E. C.

Action of Hydrochloric Acid Gas on Sulphates. By C. Hensgen (*Deut. Chem. Ges. Ber.*, **11**, 1775—1778).—Dry hydrochloric acid has no action on anhydrous ferrous sulphate at the ordinary temperature, but at a higher temperature ferric chloride, sulphur trioxide, and sulphur dioxide are formed. When hydrochloric acid is passed into a saturated solution of ferrous sulphate, ferrous chloride separates out, and the mother-liquor deposits tabular crystals of the salt $FeSO_4.6H_2O$. W. C. W.

Action of Hydrochloric Acid on Double Sulphates. By C. Hensgen (*Deut. Chem. Ges. Ber.*, **11**, 1778—1781).—When hydrochloric acid is passed into a saturated solution of potassium-copper sulphate, green crystals separate out, having the composition $K_2CuCl_4 2H_2O$.

The compounds $K_4Fe_2Cl6 + 2H_2O$ and $(NH_4)_4Fe_2Cl_{10} + 2H_2O$ were obtained by the action of hydrochloric acid on concentrated solutions of potassium and ammonium iron alums. W. C. W.

Hypophosphoric Acid and its Salts. By T. Salzer (*Liebig's Annalen*, **194**, 28—39).—An abstract of the earlier part of this research appeared in this Journal, 1877, **2**, 702.

Some further observations are first made on the formation of the above acid. The oxidation of the phosphorus is much assisted, if large quantities are left to the action of the air and water in the same space. This is effected, probably not by rise of temperature, but by the stronger ozonising of the air, or otherwise by the more active formation of hydrogen peroxide, for the phosphorus is most corroded where it dips into the liquid. It is also remarked that the formation of the hypophosphoric acid proceeds with that of the phosphorous and phosphoric acids in a certain ratio, until the liquid becomes so concentrated that no more of the first acid can be formed: only about $\frac{1}{15}$th part of the phosphorus is converted into hypophosphoric acid, phosphoric acid being the chief product. With regard to his former statement, the author now says that hypophosphoric acid decomposes both sodium chloride and sodium sulphate. The formation of crystals of the acid sodium salt only requires more time, if the solution is not very concentrated. The salt can be directly prepared by leaving sticks of phosphorus partially immersed in dilute solution of sodium chloride (*e.g.*, 1 : 100), and allowing oxidation to take place.

Sodium-compounds of Hypophosphoric Acid. Neutral Hypophosphate, $Na_4(PO_3)_2 + 10H_2O$.—If to a solution of 1 part of the acid salt in 50 parts of water, a concentrated solution of 1 part of soda is added, the solution remains clear, but if soda solution be gradually added, beautiful prismatic, needle-shaped crystals separate, consisting of the neutral

salt, and belonging to the monoclinic system. Observed faces 0P, $2\breve{P}\infty$, ∞P, P, $\frac{1}{2}$P. Cleavage parallel to $\infty\breve{P}\infty$.

The neutral salt is rather less soluble in water than the acid salt, viz., in 50 times the quantity. The cold saturated solution turns turmeric paper brown, and concentrated soda solution precipitates from it the unaltered neutral salt.

Trisodium-hydrogen Hypophosphate, $Na_3H(PO_3)_2 + 9H_2O$.—Obtained by acting with less than one part by weight of crystallised sodium carbonate on one part of the acid sodium hypophosphate in solution. The solution of this salt has an alkaline reaction. It loses its water of crystallisation at 100°. At higher temperatures it suddenly takes fire, and burns with a steady flame (phosphoretted hydrogen gas being liberated). The crystals belong to the monoclinic system, and are of a glassy lustre. They are mostly of tabular form, through a predominating 0P.

Acid Potassium Hypophosphate, $K_2H_2(PO_3)_2 + H_2O$.—Pure hypophosphoric acid neutralised with potassium carbonate and evaporated to syrupy consistency, gave crystalline nodules, which have not yet been analysed. On adding an equal quantity of acid, crystals of the above salt were obtained. It is soluble in double its weight of water at the ordinary temperature, but is not soluble in alcohol. On heating, it decomposes and gives off hydrogen which burns, whilst insoluble potassium metaphosphate is left behind. It crystallises in the rhombic system. The crystals are small, transparent, and colourless, and a combination of prism ∞P with pyramid $2\breve{P}2$; subordinate $\infty\breve{P}\infty$, $\breve{P}\infty$ and 0P. The normal potassium salt could not be obtained pure. A concentrated solution of this salt was used successfully to detect 0·003 soda, which had been dissolved in 1 c.c. of water, and existed as chloride or sulphate.

Hypophosphoric acid produces a crystalline precipitate in a solution of lithium carbonate, soluble in water with great difficulty, but easily soluble in excess of hypophosphoric acid.

Neutral Ammonium Hypophosphate, $(NH_4)_4(PO_3)_2 + H_2O$.—Obtained by heating a 5 per cent. solution of the acid with excess of ammonia. The crystals begin to fall or effloresce immediately after drying, and so could not be measured. They appear to consist of prismatic columns, with pyramidal-faced ends, and are soluble in 30 times their weight of water, the solution reacting strongly alkaline. By evaporation, ammonia is driven off, the solution soon acquires an acid reaction, and at last furnishes the acid ammonium hypophosphate. The neutral salt loses ammonia even on standing in the air, and the clear crystals assume a turbid or milky appearance. On warming they melt, with strong evolution of ammonia, and at last with combustion of the liberated hydrogen. This latter property is peculiar only to the acid hypophosphates.

Acid Ammonium Hypophosphate $(NH_4)_2H_2(PO_3)_2$.—If the solution of the previous salt be boiled until ammonia ceases to escape, the acid ammonium salt is formed, and may be obtained in needles; it is isomorphous with the acid potassium salt.

Neutral Barium Hypophosphate, $Ba_2(PO_3)_2$.—This salt is thrown down from a solution of neutral sodium hypophosphate by barium

chloride as an apparently amorphous precipitate. It is very slightly soluble in water, also in acetic acid, more soluble in hydrochloric and hypophosphoric acids. It is anhydrous, and when heated passes over into reddish barium pyrophosphate without any appearance of combustion. Even by very rapid heating of the damp neutral barium salt, it is not possible to effect the oxidation of the hypophosphoric acid by means of the oxygen of the air.

Acid Barium Hypophosphate, $BaH_2(PO_3)_2 + 2H_2O$.—Prepared from the acid sodium salt by precipitation with barium chloride. On mixing hot solutions of 4 parts of acid sodium salt in 180 parts of water, and of 5 parts of barium chloride in 10 parts of water, and immediately filtering, beautiful crystals were obtained on cooling. They belong to the monoclinic system, and are needles formed of 0P and $\infty P\infty$. They are clear, but become turbid on heating under water. They give a solution with 1,000 parts of cold water, which reacts acid, and becomes turbid on boiling in consequence of the separation of neutral or basic barium hypophosphate. The crystals scarcely suffer any loss in weight by heating at 100°, but at 140° slowly lose the 2 atoms of water of crystallisation, and at higher temperatures pass, with combustion of escaping hydrogen, into barium metaphosphate, which fuses to a white bead.

Neutral Calcium Hypophosphate, $Ca_2(PO_3)_2 + 2H_2O$.—In neutral calcium solutions, neutral sodium hypophosphate even of 200,000-fold dilution, gives rise to a perceptible turbidity. With greater concentration the solution assumes alkalinity, and all the calcium is precipitated. On the contrary, on adding calcium chloride to the sodium salt, the alkaline reaction disappears with completed precipitation of the hypophosphoric acid.

After washing, the original very gelatinous precipitate quickly becomes denser, granular, and appears under the microscope as rounded, but non-crystalline particles, and by continued washing suffers another change, whereby it becomes so finely divided as to go through the densest double or triple filters. It is insoluble in water and almost insoluble in acetic acid, but easily soluble in hydrochloric and hypophosphoric acids.

The crystallisation-water is most difficult to determine, as it begins to pass off at 100°, although the salt must be brought to 200° before all can be driven off, and then slight decomposition (*i.e.*, oxidation) ensues.

Acid Calcium Hypophosphate could not be obtained in the solid form, as neither the dilute nor the concentrated hypophosphoric acid would dissolve as much neutral calcium salt as is necessary for the formation of the acid salt. The author finally points out that as only one lime compound of this acid appears to exist, it will be possible to titrate neutral calcium solutions by means of neutral sodium hypophosphate, after addition of red litmus tincture. Alkaline reaction sets in after completed precipitation. The same remark applies to salts of lead and other metals. W. S.

Preparation of Salts in a Finely Divided State. By R. Böttger (*Chem. Centr.*, 1878, 560).—Salts which are insoluble, or only slightly soluble, in alcohol, may be obtained in a very finely divided

state by dissolving them in boiling water and pouring the concentrated solution drop by drop into alcohol. M. M. P. M.

Green and Blue Ultramarine. By G. H. Philipp (*Liebig's Annalen*, **191**, 1—12).—This paper contains the results of the further application of the author's method (*Ann.*, **184**, 132) to the comparative investigation of these products. It is shown that all varieties of blue ultramarine prepared in the wet way by the action of reagents, *e.g.*, water (in sealed tubes), zinc sulphate, ammonium chloride, boric acid, upon the green, resemble the latter in their decomposition by acids. In the dry way green is readily converted into blue ultramarine (1) by fusion with ammonium chloride. The composition of the product is essentially that of the ordinary blue variety. If the access of air be prevented as much as possible, its composition approximates somewhat to that of the green. In all cases water dissolves some NaCl from the fused mass. (2.) By heating in chlorine gas. This product also closely resembles the ordinary blue varieties. The chemistry of the conversion of green into blue ultramarine consists essentially in the oxidation of its sulphur (to SO_2 or S_2O_2); this is proved by the accompanying comparative analyses, and indirectly by the change in composition of the blue variety brought about by heating it in a current of hydrogen, when it approximates closely to that of the green, the colour remaining unchanged. The author also finds that on heating blue ultramarine (Marienberg) over the blowpipe, the air being as far as possible excluded, it is converted into a green mass having the composition of the ordinary green variety. In conclusion, he states, as the principal result of his investigation, that the chemical difference between these two ultramarines is the sodium sulphide contained in the green variety. C. F. C.

Ultramarine. By R. Hoffmann (*Liebig's Annalen*, **194**, 1—22).—In the earliest researches on ultramarine, it was observed that, on decomposing it with acids, a part of the sulphur contained in the colour was precipitated, whilst another part escaped as hydrogen sulphide, and later, that green ultramarine furnished relatively more hydrogen sulphide and less free sulphur, than blue ultramarine; and it was believed also that in green ultramarine there was, besides the alumino-sodium silicate, a lower, and in blue ultramarine a higher sulphide of sodium, or that blue ultramarine contained more sulphur than the green. The oldest researches made with ultramarine poor in silica, do not harmonise with this, for they showed that these percentages were about equal, and afterwards when ultramarines rich in silica were prepared, the blue ultramarine richer in sulphur was looked on as the higher step of sulphurisation of the green ultramarine, and it was assumed that the green variety in the refining-roasting process with sulphur passed, with absorption of sulphur, into the blue.

Although much has been done towards clearing up this intricate subject, the time has not yet come for a well-founded theory of the chemical constitution of the ultramarine compounds, or of the cause of their different colours. The author therefore intended his essay merely as a contribution towards a true theory of the ultramarine compounds, to be framed at some future time.

By fusing sulphur with sodium oxide or carbonate, or by reduction of the sulphate, the following reactions take place, disregarding intermediate compounds, which may be formed,

$$Na_2S + 4S = Na_2S_5 5Na_2S — 4Na_2 = Na_2S_5.$$

If it be assumed that there are alumino-silicates of sodium in which a part of the oxygen in closer connection with sodium is replaceable by sulphur, and that such silico-sulphides behave similarly to the free sodium monosulphide, *i.e.*, by absorption of sulphur or by giving up sodium, higher sulphides can arise without the whole silico-sulphide being decomposed, then these assumptions suffice to explain the formation of the ultramarines by the known methods of preparation, their chemical behaviour generally, and their relations to one another. The following shows this for the ultramarines poor in silica.

The composition of the pure air-dried kaolin is expressed by the formula (Rammelsberg) $H_2Al_2Si_2O_8 + Aq$, or $H_4Al_2Si_2O_9$. If an intimate mixture of kaolin and sodium carbonate be ignited just as the ordinary ultramarine mixture is (30 parts dry clay to 18 of sodium carbonate), a complete combination of the clay with soda takes place, and the composition of the combined mass may be represented as $Na_2Al_2Si_2O_8$, or sodium alumino-silicate. Now it is considered that this compound may be regarded as the silicate actually contained in the ultramarine compounds poor in silica, and that by taking up sodium, sulphur compounds it is converted into ultramarine. In fact, very good ultramarine is obtained on treating the fused mass with an excess of soda, sulphur, and resin, and submitting to the roasting process as with ultramarine. If clay at a high temperature and with proper exclusion of air be ignited with an excess of sodium sulphate and charcoal, or with soda, sulphur, and charcoal, the clay saturates itself with soda, and then this compound becomes united with sodium sulphide, forming the *white ultramarine* of Ritter. The *white ultramarine* is represented as $Na_4Al_2Si_2O_8S$ or $Na_2Al_2Si_2O_8 + Na_2S$. Thus one-half of the water in the air-dried clay appears to be replaced by Na_2O, and the other by Na_2S. White ultramarine of this purity must contain the whole sulphur as monosulphide, and by decomposing it with acids yield it as hydrogen sulphide without deposition of sulphur. Such a pure ultramarine has never been obtained; but that prepared by the author gave for *two* of sulphur as hydrogen sulphide, *one* as sulphur itself. Ritter obtained the proportion 3 : 1. From the great difficulty of obtaining white ultramarine in the pure state, the analytical numbers only approximate to those required by the formula—

White Ultramarine.

Si_2.	Al_2.	Na_4.	S.	O_8.
15·4	15·0	25·4	8·9	35·3 (calculated)
18·2	16·6	19·0	6·1	39·7 (Ritter)
17·0	16·6	21·5	6·5	38·4 (Hoffmann)

If sodium be extracted from the white ultramarine, the latter passes, with continual colour-change, through yellow and green, gradually into blue ultramarine without further process or addition. The means employed are, oxygen in presence of free sulphur, or chlorine

alone. The extracted sodium then goes out either as sulphate or as chloride. In this removal of sodium, the mode of combination of the sulphur changes in the same way as with the free sodium monosulphide under corresponding conditions, somewhat after the manner of the formula, $3Na_2S - 2Na_2 = Na_2S_3$ or $5Na_2S - 4Na_2 = Na_2S_5$. It appears very doubtful if the green ultramarine is a true chemical compound. Theoretically, it is an intermediate body between the white and the blue, and probably nearer the latter than the former. With the object of throwing light upon the constitution of the intermediate product, the blue ultramarine was investigated. The iodine method gave the proportion $Sa : Sb$ exactly as 1 : 3, or in reference to sodium sulphide one must assume in blue ultramarine Na_2S_4. If it be conceded that the passage of white into blue ultramarine rests on removal of sodium, then the blue ultramarine is formed by removal of 3 molecules of sodium from 4 molecules of the white ultramarine.

$$\underset{\text{White ultramarine.}}{Na_{16}Al_8Si_8O_{32}S_4} - Na_6 = \underset{\text{Blue ultramarine.}}{Na_{10}Al_8Si_8O_{32}S_4}.$$

$$\underset{\text{White ultramarine.}}{4(Na_2Al_2Si_2O_8 + Na_2S)} \quad \underset{\text{Blue ultramarine.}}{4(Na_2Al_2Si_2O_8) + Na_2S_4}$$

Blue Ultramarine.

Si_8.	Al_8.	Na_{10}.	S_4.	O_{32}.
17·0	16·6	17·6	9·8	39·0 (calculated)
18·2	16·1	17·3	8·4	40·0 (found)

In the formula of blue ultramarine, the whole of the sulphur is assumed to be in the state of polysulphide, whereas it has been long known that decomposition with acids liberates oxysulphur-compounds. The quantity of these present, however, is very small and variable. The author believes that these oxysulphur-compounds are most probably present together with this in chemical silicate combination; and it appears pretty certain that these oxidised sulphur-salts arise from ultramarine previously formed, and again decomposed in the burning process. These oxidised products can be formed in quantity by submitting to a too excessive oxidation; and these likewise can only be partially removed by washing.

In concluding the series of ultramarines poor in silica, a red and a yellow compound are mentioned, but these have not been closely studied, although the corresponding individuals in the series rich in silica are well known. Of this latter series less is known than the one just described. The white ultramarine here is quite wanting; the green is less positively known, and even the blue, as to purity, stands behind the one poor in silica. The large quantity of clay-residue may especially be pointed to as a reason for this. Setting out for the series rich in silica, with a silicate, $H_6Al_2Si_3O_{12}$, or $H_2Al_2Si_3O_{10} + 2Aq$ (instead of kaolin, $H_2Al_2Si_2O_8 + Aq$ in the preceding series), then with perfectly similar changes as in the latter series, the formula of the blue ultramarine rich in silica is obtained. By removal of the 2Aq in the above formula, and replacement of H_2 by Na_2, the formula $Na_2Al_2Si_2O_{10}$ is obtained, which is to be regarded as that of the rich silicate ignited with soda. Such a silicate can be

obtained by igniting a mixture of kaolin with the right proportion of silica and soda. By adding to this formula, $2Na_2S$, the type of the original silicate formula is obtained, and this transformed expression, $Na_6Al_2Si_3O_{10}S_2$ or $Na_2Al_2Si_3O_{10} + 2Na_2S$, must be that of the unknown white ultramarine of the series. Attempts to prepare this by the author and Ritter led to bluish or greenish-blue products, which appeared to stand between the white and the blue ultramarines. By abstraction of $3Na_2$ from 2 mols. of the hypothetical white ultramarine, the formula of the blue rich in silica is obtained:—

$$\underset{\substack{2(Na_2Al_2Si_3O_{10}) + 2Na_2S \\ \text{White ultramarine.}}}{Na_{12}Al_4Si_6O_{20}S_4} - Na_6 = \underset{\substack{2(Na_2Al_2Si_3O_{10}) + Na_2S_4 \\ \text{Blue ultramarine.}}}{Na_6Al_4Si_6O_{20}S_4}.$$

Blue Ultramarine (rich in Silica).

Si_6.	Al_4.	Na_6.	O_{20}.	S_4.
19·5	12·5	16·0	37·1	14·9 (calculated)
19·0	12·7	17·4	37·3	13·6 (blue ultramarine)
17·7	13·8	17·7	38·6	12·2 (bluish-green ultramarine)

Now in this series, two products are found, namely, a red and a yellow compound. The first has only been recently prepared in the pure state, and was at first only designated "violet ultramarine." It now appears that the vapours of different mineral acids at a temperature of 150° behave quite differently towards blue ultramarine from the aqueous solutions of the same acids at temperatures below 100°. If, for example, dry hydrochloric acid gas be passed over heated blue ultramarine, with exclusion of air, there appears to be no action; but in presence of air or of other oxidising agents, the blue ultramarine passes gradually into a violet, and with long-continued action into an intensely rose-red coloured substance, without liberation of hydrogen sulphide or other sulphur-acids in any considerable quantity. The whole of the sulphur of the blue ultramarine appears to pass over into the new compound. On washing, sodium chloride and some alumina pass into solution. Analysis shows that the only difference between the washed and dried substance and blue ultramarine, is that the amount of sodium has been diminished about one-fourth, and that the manner of combination of the sulphur has been altered by the passage of the white ultramarine of Ritter past the green to the blue, *i.e.*, *a*-sulphur is considerably diminished, *b*-sulphur almost unaltered, *c*-, *d*-, and *e*-sulphur somewhat increased (*c*-, *d*-, and *e*-sulphur refer to the sulphur taken at first to be as *a* and *b*, and so determinable by the iodine method, but by slight subsequent decompositions in the operations, &c., converted into oxidised sulphur compounds. Thus the total sulphur would be a and $b + c + d + e$). The proportion of $Sa : Sb$ is exactly 1 : 4, viz., that of the sodium pentasulphide, Na_2S_5. From many observations on the physical behaviour of the red ultramarine, especially in the grinding and washing, also in the chemical fact of the solution of some alumina, it is concluded that the chemical process in the preparation does not go quite smoothly, and that the best product yet obtained is still farther from the condi-

tion of chemical purity than the blue ultramarine. Theoretically, the red ultramarine is obtained by abstracting $8Na_2$ from the 5-fold formula of the hypothetical white (rich) ultramarine. It may also be obtained by abstraction of Na_2 from the 5-fold formula of the blue (rich) ultramarine :—

$$Na_{30}Al_{10}Si_{15}O_{50}S_{10} - Na_{16} = Na_{14}Al_{10}Si_{15}O_{50}S_{10}.$$

$5(Na_2Al_2Si_3O_{10} + 2Na_2S)$ — White ultramarine (rich in silica).

$5(Na_2Al_2Si_3O_{10}) + 2Na_2S_5$ — Red ultramarine (rich in silica).

$$Na_{30}Al_{20}Si_{30}O_{100}S_{20} - Na_2 = Na_{28}Al_{20}Si_{30}O_{100}S_{20}$$

$5[2(Na_2Al_2Si_3O_{10}) + Na_2S_4]$ — Blue ultramarine (rich in silica).

$2[5(Na_2Al_2Si_3O_{10}) + 2Na_2S_5]$ — Red ultramarine (rich in salica).

S_{15}.	Al_{10}.	Na_{14}.	O_{50}.	S_{10}.
19·7	12·8	15·0	37·5	15·0 (calculated)
20·2	13·5	12·9	37·9	15·5 (violet, Nürnberg)
18·8	13·8	14·1	37·0	16·3 (red, of Büchner)

Yellow ultramarine is obtained with the red as an accidental product, but recently Grünzweig has found a sure method of preparing of it from the red ultramarine. A formula can be derived from that of the blue ultramarine (rich), by abstracting one-fourth of the sulphur, and adding oxygen equivalent to the total sulphur in the blue ultramarine, thus :—

$$Na_6Al_4Si_6O_{20}S_4 = 2(Na_2Al_2Si_3O_{10}) + Na_2S_4$$

Blue ultramarine (rich).

$$Na_6Al_4Si_6O_{21}S_3 = 2(Na_2Al_2Si_3O_{10}) + Na_2S_3O_4.$$

Yellow ultramarine (rich).

$$Na_6Al_4Si_6O_{24}S_3 = Na_6Al_4Si_6O_{20}S_4 - S + O_4.$$

Yellow Ultramarine (*rich in silica*).

Si_6.	Al_4.	Na_6.	O_{24}.	S_3.
18·8	12·1	15·4	42·9	10·8 (calculated)
18·8	13·0	13·7	42·7	11·8 (found)

The decomposition-products were only free sulphur and sulphuric acid, so that no iodine was required. This yellow ultramarine is, as Grünzweig shows, an oxidation product of blue.

The following formulæ are intended to show in their arrangement, &c.—

(1.) In what series of reactions ultramarine can arise from aluminosilicates by the known method of preparation.

(2.) In what relation the different ultramarine compounds stand to each other.

(3.) How they join themselves to those groups of the mineral silicates, which originally stimulated the artificial preparation of ultramarine.

Series poor in Silica.

Kaolin	$H_2Al_2Si_2O_8 + H_2O$
Kaolin ignited with soda	$Na_2Al_2Si_2O_8$
White ultramarine	$Na_2Al_2Si_2O_8 + Na_2S$
Blue ultramarine	$4(Na_2Al_2Si_2O_8) + Na_2S_4$
Nosean	$2(Na_2Al_2Si_2O_8) + Na_2SO_4$
Hauyu	$2\left(\begin{matrix}Na\\Ca\end{matrix}\right\}_2 Al_2Si_2O_8) + \left.\begin{matrix}Na\\Ca\end{matrix}\right\}_2 SO_4$
Fresh sodalite	$3(Na_2Al_2Si_2O_8) + 2NaCl$

Series rich in Silica.

Hypothetical root silicate	$H_2Al_2Si_3O_{10} + 2H_2O$
The same ignited with soda	$Na_2Al_2Si_3O_{10}$
Mesotype (natrolite)	$Na_2Al_2Si_3O_{10} + 2H_2O$
Decomposed sodalite	$Na_2Al_2Si_3O_{10}$ (traces of NaCl)
Hypothetical white ultramarine	$Na_2Al_2Si_3O_{10} + 2Na_2S$.
Blue ultramarine	$2(Na_2Al_2Si_3O_{10}) + 2N_2S_4$
Red ultramarine	$5(Na_2Al_2Si_3O_{10}) + 2Na_2S_5$
Yellow ultramarine	$2(Na_2Al_2Si_3O_{10}) + Na_2S_3O_4$

W. S.

The Gadolinite-Earths. By C. Marignac (*Ann. Chim. Phys.* [5], **14**, 247).—Working on about 300 grams of the mixed oxides, the author, following out the method of separation adopted by Bahr and Bunsen, succeeded in separating the oxides into eighteen different portions, passing from pure yttria on the one hand to pure erbia on the other. The yttria and erbia present all the properties previously assigned to them by Bunsen and Bahr, and by other observers. The original mixture of oxides was of a pale yellow colour, and it was found that, whereas yttria is white and erbia is pale rose-coloured, the intermediate portions of the oxides were of a more or less deep yellow colour as they were further removed from erbia on the one hand, and from yttria on the other. The most deeply-coloured portion was examined, with the view of settling the question, whether this colour is due to didymium or to some other oxide of the yttrium family.

Its solution in nitric acid presented the absorption-spectra of erbium and didymium. By treatment with potassium sulphate a small quantity of didymium was separated, after which the absorption-spectrum of didymium was no longer visible, although the colour of the oxide had suffered no perceptible diminution. It must therefore be concluded that the colour of this oxide is not due to didymium, since it was proved by experiment that a mixture of yttria and erbia neither prevents the precipitation of didymium nor affects its absorption-spectrum; and since neither yttria nor erbia is yellow, the colour of the oxide must be due to the third gadolinite-earth, terbia, originally distinguished by Mosander, and the existence of which was denied by Bunsen and Bahr, and more recently by Cleve and Höglund.

For the separation of terbia in a state fit for examination, those portions of the mixed oxides must be taken in which traces only of

erbia exist. The oxides are dissolved in nitric acid, and subjected to a series of fractional precipitations with oxalic acid, the first portions of precipitate being the richest in terbia. By this treatment the whole of the yttria is separated, and the terbia obtained mixed only with didymium oxide and erbia. The didymium is separated in the usual way by means of potassium sulphate; but for the separation of terbia from erbia no method has yet been discovered. The molecular weight of terbia (mixed with erbia) is 116, and estimating the amount of erbia at 6—8 per cent., and taking its molecular weight at 129, the real molecular weight of terbia must be about 115, which would make the atomic weight of terbium either 99 or 148·5, according as the oxide is considered as a monoxide or as a sesquioxide. This atomic weight was confirmed by a determination made on pure terbia obtained from the formate (see next abstract).

Terbium oxide, after moderate heating, is of a pure dark orange-yellow colour; it is decolorised by heating in a current of hydrogen, or by simple exposure to a very high temperature; in the latter case it is not reoxidised by heating in contact with oxygen. This loss of colour is accompanied by an extremely slight loss of weight, as in the case of didymium oxide. Terbium oxide dissolves slowly, but completely, in very dilute acids, in hydrochloric acid with disengagement of chlorine. Its salts are colourless, and have no absorption-spectrum.

Terbium sulphate, $Tb_2(SO_4)_3 8H_2O$, forms colourless crystals, isomorphous with the sulphates of yttrium, erbium, and didymium; the crystals lose all their water at a low red heat, and their sulphuric acid at a higher temperature.

The yellow mixture of oxides from the decomposition of the nitrates, which contained erbia in large quantities, was submitted to fractional precipitation with oxalic acid. By this method the whole of the yttria may be separated and an oxide obtained, whose equivalent rises gradually by continuation of the above treatment, but the colour of which never attains the intensity of pure terbia, and even seems to diminish after a time. The oxalate from this oxide has a decided rose colour, and its solutions show the erbium absorption-bands very plainly.

This and the following facts seem to point to the existence of a fourth oxide of this family.

Although the yellow oxide obtained in the above experiment could not contain more than a trace of yttria, and although it contained erbia to the extent of probably half its weight, its molecular weight was only 117, which is much lower than would be expected of a mixture in equal proportions of erbia and terbia, whose respective molecular weights are 129 and 115.

Terbium formate, as stated by Delafontaine (next abstract), is much less soluble than the formates of yttrium and erbium. When, however, the author attempted to separate the above mixture of oxides by this method, he obtained only a series of products differing but slightly in their molecular weights and depths of colour.

C. W. W.

Terbium and its Compounds, and the probable existence of a New Metal in the Samarskite of N. Carolina. By M. Delafontaine (*Ann. Chim. Phys.* [5], **14**, 238).—Terbium is most ad-

vantageously extracted from samarskite, which contains but small quantities of yttria and of Bunsen's erbia. The oxides precipitated by means of potassium sulphate contain but little cerium, and probably no lanthanum, the didymium being accompanied by terbium in some quantity. The mixed oxides were dissolved in nitric acid, and reprecipitated by potassium sulphate. The bases contained in the mother-liquor from this precipitate were combined with acetic acid, the acetate thus formed crystallising in colourless crystals, easily decomposed by heat, giving a dark-orange oxide. Treated with formic acid this oxide gave an indistinctly crystalline crust more soluble than the formates of the cerium metals, and the mother-liquor, evaporated to dryness, intumesced greatly when heated, a character not exhibited by the formates of lanthanum and didymium.

The following process is the one finally adopted for the preparation of terbia. After separation of the cerium metals by potassium sulphate, the syrupy solution of the nitrates of the yttrium metals was mixed with a saturated solution of sodium sulphate, and crystals of the same salt were added until no more was dissolved. The crystalline deposit thus formed furnishes a dark yellow oxide, that of the soluble sulphate being lighter-coloured.

The nitric acid solution of the dark yellow oxide was fractionally precipitated by oxalic acid, and the least soluble portions of the oxylate were converted into formate. The insoluble portion of the formate thus produced furnished a dark orange-coloured oxide; by repeating this treatment the percentage of base in the formate may be raised above 60 per cent. The solubility of the formate is about 3·3 parts in 100 parts of water.

The atomic weight of terbium is fixed provisionally at 98, the molecular weight of the oxide being 114.

Terbium formate is a white powder, or forms a strongly adherent non-crystalline crust, soluble in about 30 times its weight of water. When heated it burns without intumescence. The acetate crystallises in small, transparent, colourless prisms, much less soluble than acetate of didymium. Its formula is $Tb(C_2H_3O_2)_2 + 2\frac{2}{3}$ Aq. It chars below redness, and burns like tinder.

The slight solubility of terbium formate, and the fact that it is extracted from a double sulphate insoluble in sodium sulphate, might confound terbium with lanthanum and didymium. The formation, on the other hand, of the oxalate in presence of a large excess of nitric acid, excludes the possibility of the presence of an appreciable quantity of lanthanum; moreover, the spectroscope shows only a trace of didymium. The absence of colour in the salts, and the difference of solubility of the formates, acetates, and sulphates of terbium and didymium, also distinguish the two metals.

The terbia described in the present paper possesses the properties previously recognised in Mosander's erbia. This is seen in its behaviour to acids; its loss of colour when heated out of contact with air, and recovery of colour when heated in contact with oxygen; its great tendency to form sub-salts insoluble in nitric acid, acetic acid, &c. The only important difference is the slightly higher molecular weight, which is probably due to the imperfect purity of the former product.

On the other Earths of Samarskite.—As mentioned above, sodium sulphate separates the oxides of the yttrium metals of samarskite into two portions, one of darker, the other of lighter colour. The mixture of oxides was treated with hot formic acid diluted with a quantity of water calculated to dissolve the salts produced; a white magma was, however, formed, which was not dissolved by addition of more hot water. The liquid from this deposit yielded on evaporation, first, brilliant, well-defined rhomboïdal prisms, not grouped together; they contained 47 to 47·5 per cent. of a bright yellow oxide; afterwards the liquid yielded longer prisms, arranged in fan-like groups; these last, mixed with the dried mother-liquor, gave on heating, during which they intumesced greatly, a light yellow oxide, which was put aside as rich in yttria. The first formates, purified by recrystallisation, conversion into oxalate, and digestion with nitric acid, contained a base whose equivalent (molecular weight) varied between 89 and 91. The oxide, divided into two portions, one of which was converted into acetate, and the other into formate, gave on mixing a slightly soluble white powder, the molecular weight of whose base was also about 91.

The dark-yellow oxides remaining after the extraction of terbia were subjected to a repetition of the process for the extraction of terbia, and the portions not precipitated by oxalic acid, treated in the above manner, gave a white crystalline powder, the molecular weight of whose base was also about 90.

The author has also observed a number of other circumstances, which lead him to believe in the existence of a new earth in samarskite, besides those already described. C. W. W.

Philippium. By M. Delafontaine (*Compt. rend.*, **87**, 559).—In a previous paper the author indicated the probable existence of a fourth earth in samarskite. This new earth is intermediate in colour and molecular weight between yttria and terbia (YO = 74·5 : TbO = 114). Assuming that philippia is a protoxide, its equivalent is between 90 and 95; it is easily obtained free from all but a small quantity of yttria, and a somewhat larger proportion of erbia.

Philippium formate crystallises easily, either on cooling, or by spontaneous evaporation, in small shining rhomboïdal prisms, less soluble than yttrium formate, which is deposited in nodular groups from a syrupy solution; terbium formate is anhydrous and soluble in 30—35 parts of water. Sodio-terbic sulphate is scarcely soluble in water, the corresponding philippium-compound is easily soluble. Philippium oxalate is more soluble in nitric acid than terbium oxalate, but less soluble than the yttrium salt. Philippium nitrate becomes dark yellow when fused; yttrium and terbium nitrates remain colourless. Philippium salts are colourless when pure; the oxide is decolorised by heating in a current of hydrogen, or simply by a strong heat, becoming yellow again on cooling in the air. Concentrated solutions of philippium salts give in the indigo-blue ($\lambda = 450$ nearly) a wide and very intense absorption-band, with its edges, more especially the right, very well defined; this band is not seen in yttrium, erbium, or terbium solutions. In the green there are two rays, one belonging to erbium, the other and less refrangible, probably to philippium; finally, in the red there is

at least one narrow band. On directing the slit of the spectroscope towards the sun, the author observed, with solutions of terbium, a moderately dark band in the violet ($\lambda = 400$—405 nearly); its breadth is about half that of the band characteristic of philippium, and it seems to be entirely wanting in some specimens of terbia, others having merely a trace. The author doubts whether it is really characteristic of terbium, and considers it possible that it may indicate another new earth, whose atomic weight would be intermediate between those of erbium and terbium. He intends to study this question more fully, and also promises a comparative study of philippium and terbium compounds. C. W. W.

The Mosandrium of J. L. Smith. By M. Delafontaine (*Compt. rend.*, **87**, 600).—The author considers that Lawrence Smith's mosandrium is identical with the terbium which he himself described in a recent memoir (*Ann. Chim. Phys.* [5], **14**, 238) (see p. 115). He claims also the priority of discovery, since "mosandrium" is but a mixture of about 75—80 per cent. terbium with 20—25 per cent. of a mixture of yttrium, erbium, and philippium. C. W. W.

Decipium, a new Metal from Samarskite. By M. Delafontaine (*Compt. rend.*, **87**, 632).—In his researches on the samarskite of N. Carolina the author has discovered a new metal, which he calls *decipium* (from *decipiens*, deceptive). This metal, which otherwise possesses the properties characteristic of the metals of the cerium and yttrium families, forms an oxide whose molecular weight is approximately 122 for the formula DpO, or 366 for Dp_2O_3; it has not yet been sufficiently separated from didymium to be able to show its true colour; its salts are colourless; the acetate crystallises easily, is less soluble than the didymium salt, but more so than the terbium salt; decipio-potassium sulphate is but slightly soluble in a saturated solution of potassium sulphate, but easily soluble in pure water.

Decipium nitrate gives an absorption-spectrum containing at least three bands in the blue and indigo. It is necessary to use direct solar light. The most refrangible band is a little narrower than that of philippium or the band *m* of didymium; it is tolerably dark; its middle corresponds nearly with the wave-length 416, or with No. 195 on Lecoq's scale; it is approximately in the middle of the space between Fraunhofer's lines G and H, but a little nearer to G. Neither didymium nor terbium gives bands in this part of the spectrum; the band characteristic of terbium is more to the right, and nearly out of the spectrum given by ordinary light. Under exceptional circumstances the author observed the violet space beyond this band, and distinguished two well-defined bands, probably H and H′.

The second decipium band is narrower, more intense, and less well-defined; it is situated in the less refrangible blue, and its middle corresponds with the wave-length 478; it is nearly in the same place as one of the didymium bands, but is much darker. Finally, more to the left, and nearer the limit of blue and green, there is an ill-defined minimum of transmission, which is possibly composed of two faint bands. Samarskite therefore contains the following metals:—

Name.	Colour of oxide.	Mol. weight.	Characteristic absorption-band in λ.
Yttrium	White.....	YO = 74·5	None
Erbium	Rose	EbO = 130*	520—522
Terbium	Orange	TbO = 114—115	400 (about)
Philippium ..	Yellow	PpO = 90	449 „
Decipium ..	White (?) ..	DpO = 122	416
Thorinum ..	White.....	ThO_2 = 267·5	None
Didymium ..	Brownish ..	DiO = 112—114	572—577
Cerium	Pale yellow .	C_2O_3 = 324	None

The atomic weights of some of these metals present a curious relationship:

Yttrium	=	58
Philippium	=	74 or 58 + 2 × 8
Terbium	=	98 or 58 + 5 × 8
Decipium	=	106? or 58 + 6 × 8
Erbium	=	114 or 58 + 7 × 8

If these metals are taken as trivalent (Y_2O_3, Tb_2O_3, &c.) the difference would be 12 or one of its multiples, instead of 8.

C. W. W.

Ytterbium, a new Metal from Gadolinite. By C. Marignac (*Compt. rend.*, **87**, 578).—In the course of his researches on the gadolinite-earths (*Ann. Chim. Phys.* [5], **14**, 247) the author obtained, by the method there described, some quantity of an earth whose physical and chemical characters and molecular weight were those of erbia. On continuing the process of separation by fusing the nitrate, he finds, however, that a further separation takes place, resulting, on the one hand, in a rose-coloured earth presenting the characters of erbia somewhat intensified, and on the other hand, in a colourless earth, of molecular weight = 131 nearly.

The metal contained in this new earth the author names *ytterbium*; it presents the following characters:—Both the oxide and the salts are colourless; the nitrate is decomposed by heat without coloration.

Solutions of ytterbia give no absorption-spectrum, either in the ordinary spectrum or in the ultra-violet (Soret). The earth itself is less easily attacked by acids than the other earths of this family. It dissolves slowly in the cold, or at a gentle heat in slightly diluted acids; on boiling, it dissolves easily even in acetic and formic acids. Ytterbium sulphate resembles, and is probably isomorphous with, the sulphates of yttrium and erbium; it dissolves easily and without residue in sulphate of potassium, no precipitate being formed even on boiling. A neutral and not too concentrated solution of ytterbium chloride is not precipitated by sodium thiosulphate; a very concentrated solution, containing erbium, gives a precipitate containing a larger proportion of erbium than is contained in the residual salts. Ytterbia precipitated by potash, and submitted to a current of chlorine, dissolves completely in presence of excess of alkali.

The formate, $Yb_2O_3.3C_2H_2O_3.4Aq.$,† dissolves in less than its weight of

* See Marignac's paper, page 119. † $(?)CH_2O_3$.

water, and crystallises in small crystalline nodules, resembling the formates of yttrium and erbium; it is decomposed with intumescence by heat, and loses its water of crystallisation at 100°. All these properties prove the absence of thorinum, the only metal which could be present and could raise the equivalent.

The existence of this new metal in erbia throws doubts on the exactness of the equivalent of the latter, as determined by Bunsen and others; it would lead to the supposition that the molecular weight of erbia must be lower than that usually given; in fact, in the purest specimen of erbia prepared (which still contains ytterbia) the molecular weight was between 122 and 126, the true molecular weight of erbia being probably lower even than this.

Taking the molecular weight of ytterbia at 131, the atomic weight of ytterbium would be either 115 or 172·5, according as we adopt the formula YbO or Yb_2O_3 for the oxide. C. W. W.

The probable Compound Nature of the Didymium from Cerite. By M. Delafontaine (*Compt. rend.*, **87**, 634).—Didymium obtained from cerite shows, as is well known, in the blue towards the green, a group of four nearly equidistant narrow bands; the first and fourth ($\gamma = 482$ and $\zeta = 469$, Lecoq) are much better defined and darker than the others. Sometimes the second, third, and fourth look like a wide minimum of transmission, in the middle of which ζ appears very distinct. Didymium from samarskite never exhibits this group of bands under any circumstances. It seems also that the band in the indigo-blue (which Lecoq calls *m*), whose middle corresponds with the wave-length 444, is always less intense in samarskite didymium than in cerite didymium.

It might be conceived that the presence of terbium and decipium in the didymium from samarskite would produce the above effects; however, when a solution of terbium was placed between the solution of didymium and the slit of the spectroscope, no effect was produced on the spectrum of the didymium.

It would seem therefore that the didymium from cerite contains a new element, characterised by the above-mentioned absorption-bands, which are wanting in the spectrum from samarskite didymium.

C. W. W.

Pyrophoric Iron. By R. Böttger (*Chem. Centr.*, 1878, 575).—By heating iron tartrate, a pyrophoric mixture of carbon and ferrous oxide is obtained. A pyrophoric form of ferrous oxide, free from carbon, may be procured by heating iron oxalate in a small glass bulb. M. M. P. M.

Cobalt-ammonium Compounds. By S. M. Jörgensen (*J. pr. Chem.* [2], **18**, 209—247).—In the present communication the author considers the *chloropurpureo-salts:* he has also succeeded in preparing analogous series of bromopurpureo-salts and nitrato-purpureo-salts: he regards the xanthocobalt salts of Gibbs and Genth as belonging to the nitro-purpureo series.

Acid Chloropurpureocobalt Sulphate, $(Cl_2.Co_2 10NH_3)_2SO_4(SO_4H)_6$, is prepared by intimately mixing 1 mol. of purpureo-chloride with about

12 mols. of concentrated sulphuric acid, and after some time treating the mixture with 40 c.c. of water at 70° for every 5 grams of purpureo-chloride used. On filtering and leaving the filtrate to cool, large dark violet prisms are deposited; they are collected on a funnel in the lower part of which is placed a small cone of fine platinum gauze, washed with strong alcohol, pressed between paper, and dried over sulphuric acid. The alcohol causes the precipitation of a small amount of a new salt (probably normal sulphate; see below), but this is washed through the platinum gauze and removed.

The crystals are very readily decomposed on the surface by water, but dissolve in warm water, with production of an acid liquid, from which cobaltic oxide is not precipitated on long-continued boiling. Inasmuch as in this and the following chloropurpureo-salts the chlorine cannot be detected by the ordinary tests, the author regards the chlorine as intimately combined, probably with cobalt, whereas the other negative radicles are in more direct combination with ammonia. The chlorine however in this salt is partially precipitated on boiling with silver nitrate. Anhydrous normal sulphate mixed with hydrated sulphate crystallises from a solution of the acid sulphate in hot water.

Normal Chloropurpureocobalt Sulphate. — *a. Hydrated Salt*, $Cl_2.(Co_2 10NH_3)2SO_4.4H_2O$. Prepared in a manner very similar to that described for the foregoing salt, only 6 mols. of sulphuric acid however being employed for each mol. of purpureo-chloride; the crystals which separate on filtering and partial cooling are removed (see below), and the second filtrate on complete cooling deposits nearly pure hydrated sulphate. The crystals are washed with cold water and pressed: they present rhombic forms, and are of a deep purple-red colour, with brilliant lustre. This sulphate is soluble in 133·4 parts of water at 17·3°, it is readily soluble in hot water; the solution unless very dilute, deposits the anhydrous sulphate on cooling. On boiling with water cobaltic oxide is precipitated. *b. Anhydrous Salt*, $Cl_2(Co_2.10NH3)2SO_4$. —The crystals which separate on partial cooling of the first filtrate (see above) consist of the salts *a* and *b* mixed: on exposure to air, *a* alone effloresces, and *b* may then be mechanically separated. This salt forms black or purple-brown octohedral crystals, which are more slowly soluble in water than the hydrated salt: the solution reacts as that of the latter salt.

Chloropurpureocobalt Nitrate, $Cl_2(Co_2 10NH_3)4NO_3$.—This salt appears to have been prepared by Gibbs (*Proc. Am. Acad.* 1876, **11**, 3), but the formula given by him is inconsistent with his own analytical results. It is best prepared by mixing the purpureo-chloride with water and a little dilute sulphuric acid, treating the mass on a filter with water at 50°, with addition at intervals of a few drops of sulphuric acid, and allowing the solution to flow into an excess of concentrated ice-cold nitric acid; the crystals which form are washed with nitric acid of sp. gr. 1·2 and finally with alcohol. The salt is soluble in about 80 parts of water at 16°. By slowly heating the solution, the corresponding roseo-salt is produced: on boiling, cobaltic oxide is thrown down. At a temperature somewhat above 110° the salt decomposes with violence.

Chloropurpureocobalt Hydrate does not appear to exist. The

author attempted to prepare this salt by treating of 1 mol. normal chloro-sulphate with 2 mols. of barium hydroxide and water in the cold; the filtrate reacted however as a mixture of roseo-cobalt chloride and hydrate. Only roseo-cobalt hydrate was obtained on treating purpureo-chloride with silver oxide and water.

Chloropurpureocobalt Bromide, $Cl_2(Co_2 10NH_3)Br_4$, may be prepared from the normal sulphate, or nitrate, by precipitating with sodium bromide, or from the carbonate, by precipitating with concentrated hydrobromic acid. The salt is however best prepared from purpureocobalt chloride by a process analogous to that used for the preparation of the nitrate, the liquid being allowed to flow into cold concentrated hydrobromic acid, in place of nitric acid; the precipitate is washed with hydrobromic acid and finally with alcohol. This salt crystallises in octohedral forms resembling the purpureo-chloride, but of a more violet-red colour than that salt. It is soluble in 214 parts of water at 14·3°. The author regards Claudet's salt $(10NH_3.Co_2)Br_6$ (*Chem. Soc. Qu. J.*, **4**, 361) as probably a bromide belonging to the roseo series.

Chloropurpureocobalt Iodide, $Cl_2.(Co_2 10NH_3)I_4$, is best prepared by a method similar to that employed for the preparation of the bromide: it crystallises from hot water containing a little hydriodic acid in large dark brownish-violet octohedrons: it is soluble in 54·4 parts of water at 15·6°. By treating a solution of this salt with iodine for some time, or by acting on the chloronitrate with iodine dissolved in potassic iodide, or by adding a hydriodic acid solution of iodine to an aqueous solution of the chloropurpureocobalt carbonate, brown metallic-like needles separate, which exert a powerful polarising action on light. These crystals could not be obtained perfectly pure; they are supposed by the author to be *chloropurpureocobalt periodide*.

Chloropurpureocobalt mercuric Chloride, Bromide and Iodide.—By treating purpureo-cobalt chloride with excess of mercuric chloride, Claudet, Carstanjen, and Gibbs obtained a salt with 6 mols. of $HgCl_2$. The same salt is obtained by using sodio-mercuric chloride, $NaHgCl_3$, or Na_4HgCl_6: the author shows that this salt is a member of the chloropurpureo series, and that the hydrated salt (with $4H_2O$) prepared from roseo-cobalt chloride is a member of the roseo series. He proposes for the latter the formula $(Co_2.10HN_3)(HgCl_3)_6'4H_2O$ where $HgCl_3 = Hg{=}Cl{-}Cl{=}Cl{-}$ and the formula $Cl_2.(Co_2.10NH3)(Hg_3Cl_8)_2''$ for the former, where $Hg_3Cl_8 = Hg{<}\begin{matrix}Cl{=}Cl{-}Hg{-}Cl{=}Cl{-}\\ Cl{=}Cl{-}Hg{-}Cl{=}Cl{-}\end{matrix}$. When a moderately warm aqueous solution of purpureo-chloride containing a little sulphuric acid is mixed with an aqueous solution of Na_2HgBr_4, large violet-red needles slowly separate. This salt is regarded by the author as having the complex formula—

$$Cl_2(Co_2 10NH_3)\left\{\begin{matrix}\text{——}(Hg_3Br_8)''\text{——}\\ (HgBr_3)' \quad (HgBr_3)'\end{matrix}\right\}(10NH_3.Co_2)Cl_2.$$

By substituting a solution of potassium iodide, saturated at 70° with mercuric iodide, for the double sodio-mercuric chloride, in the preceding process, a salt separates immediately in brownish-yellow needles, which, when quickly washed with cold water in the dark, and pressed, give numbers agreeing with the formula $Cl_2.(Co_2 10NH_3)(HgI_3)_4$.

Another salt containing mercury and iodine may be prepared by decomposing a solution of the normal chlorosulphate or nitrate with potassium iodide solution, and then adding an aqueous solution of potassiomercuric iodide, K_2HgI_4; after some time large brilliant brown plates separate. This salt appears to have the formula $Cl_2.(Co_210NH_3)(HgI_4)_2''$ where HgI_4 = —I═I—Hg═I—. It is always more or less mixed with the iodide already described.

Chloropurpureocobalt-platinic Bromide, $Cl_2(Co_210NH_3)(PtBr_6)_2$. This salt, which is the analogue of the platinic chloride salt prepared by Claudet, as also by Gibbs and Genth, separates in the form of a yellow-brown crystalline precipitate, from a moderately warm mixture of the chloronitrate and potassioplatinic bromide, both in aqueous solution. It is sparingly soluble in cold water. The crystals which separate from a mixed solution of the purpureo-cobalt chloride, or nitrate, and tin chloride, or tin-ammonium chloride, are shown to consist of purpureo-chloride only, and not to be a double cobalt salt containing tin chloride, as supposed by Gibbs and Genth (*Sill. Am. J.* [3], **23**, 264). Similarly purpureo-cobalt bromide separates from a mixed solution of the chloronitrate and potassium-zinc bromide.

Chloropurpureocobalt Silicofluoride, $Cl_2(Co_2.10NH_3)(SiF_6)_2$. This salt, which has been described by Gibbs (*Proc. Am. Acad.* **11**, 9), may be readily produced by adding a cold solution of any chloropurpureo compound, preferably the nitrate, to excess of concentrated aqueous hydrofluosilicic acid. The crystals are dichroic, and separate in rhombic plates; they are regarded by the author as without water of crystallisation. The formation of this salt may be used as a very delicate test for silicic acid in presence of hydrofluoric acid. It is only necessary to add 1 or 2 c.c. of a cold concentrated solution of chloropurpureocobalt nitrate to the suspected liquid: if 1 per cent. of silicic acid be present, crystals of the double salt separate at once; with smaller quantities of silicic acid the crystals separate only after some time. If necessary, the crystals may be washed with alcohol and examined under the microscope. The author has thus detected with certainty 1·6 mgram. of silicic acid in presence of 3·05 gram of 39 per cent. hydrofluoric acid.

Chloropurpureocobalt Dithionate, $Cl_2.(Co_210NH_3)(S_2O_6)_2$. — This salt separates as large, brilliant, violet prisms on mixing a cold aqueous solution of the purpureochloride with sodium dithionate. This salt is sparingly soluble in cold, more readily in hot water.

Chloropurpureocobalt Thiosulphate, $Cl_2.(Co_210NH_3)(S_2O_3)_2$, prepared by precipitating a cold solution of the purpureochloride with a solution of sodium thiosulphate. The salt crystallises in rhombic form, $\infty P.\breve{P}\infty$, of a brownish-red colour: it is insoluble in cold and only slightly soluble in warm water.

Chloropurpureocobalt Chromate, $Cl_2(Co_210NH_3)(CrO_4)_2$ *and Dichromate*, $Cl_2(Co_210NH_3)(Cr_2O_7)_2$. The former salt is obtained in the form of a reddish or flesh-coloured crystalline powder, by mixing cold solutions of the normal chlorosulphate, nitrate, or purpureochloride and potassium chromate. For the preparation of the dichromate, potassium dichromate solution is employed, and the temperature of the sulphate or nitrate solution is slightly raised; if purpureo chloride be employed

the solution must be cold. So soon as crystals form, the mother-liquor must be drained off, and the crystals quickly washed with cold water, and dried over oil of vitriol. If the crystals be allowed to stand for 24 hours or so in contact with a large quantity of wash-water they become much altered in form and appearance, but on analysis little or no change in composition can be detected. Chloropurpureocobalt dichromate crystallises in brilliant golden scales, which are somewhat soluble in water. The author's results concerning these chromate salts are not in keeping with those of Braun (Göttingen, 1862).

Chloropurpureocobalt Carbonate, $Cl_2.(Co_210NH_3)(CO_3)_2$, crystallises with 9 molecules of water in large beautiful violet-red crystals, and with 1 mol. of water in small 6 or 4-sided prisms of a darker violet colour. The former salt is obtained by rubbing together purpureochloride and excess of moist silver carbonate, filtering after a few minutes, at once adding alcohol until a faint turbidity is produced, leaving the solution to crystallise, and washing with alcohol of 50° (Twaddell). If the silver carbonate and purpureochloride be allowed to remain for some time in contact, or if alcohol be not added to the filtered liquid very shortly after filtration, roseocarbonate is produced. By dissolving this salt in water after efflorescence, and adding alcohol until a distinct turbidity is produced, the salt with 1 mol. of water is obtained. The 9-hydrated salt effloresces rapidly; it is very soluble in water, producing a deep cherry-red liquid with alkaline reaction.

Chloropurpureocobalt Oxalate, $Cl_2(Co_213NH_3)(C_2O_4)_2$, and *Acid Tartrate*, $Cl_2(CO_210NH_3)(C_4H_5O_6)_45H_2O$.—The former salt was obtained by Gibbs and Genth (*Sill. Am. J.* [2], **23**, 320). These chemists, however, overlooked the presence of chlorine in the salt. Krok gave the formula adopted above, which was admitted to be the true formula by Gibbs (*Proc. Am. Acad.*, **11**, 4). By using the chloronitrate as starting point in the preparation, the author has repeatedly obtained crystals of the same composition. Gibbs (*loc. cit.*) says that the composition of different preparations varies considerably.

The acid tartrate is prepared by adding a considerable excess of an aqueous solution of tartaric acid to the chlorocarbonate, followed by addition of alcohol. This salt crystallises in large brilliant violet-red needles, which are tolerably soluble in water, forming a liquid with an acid reaction.

Chloropurpureocobalt Pyrophosphate, $Cl_2(Co_210NH_3)(P_2O_7H_2)_2$, and $Cl_2.(Co_210NH_3)P_2O_7.xH_2O$.—The acid salt is prepared by precipitating an aqueous solution of the chloronitrate with sodium pyrophosphate and a little free pyrophosphoric acid. The salt crystallises in masses of brilliant violet-red needles: it dissolves with difficulty in water, forming an acid liquid, from which silver nitrate precipitates silver pyrophosphate, but no silver chloride.

The neutral pyrophosphate is prepared by adding water just sufficient for solution to a mixture of 1 molecule of the chloronitrate and rather more than 1 molecule of sodium pyrophosphate, filtering at once, and adding alcohol in small successive quantities until the greater part of the salt has crystallised out: the crystals are washed with alcohol and dried in the air. This salt crystallises in long thin needles of a violet-red colour, containing from 3 to 4 molecules of water.

Braun (*loc. cit.*) and Gibbs (*Proc. Am. Acad.*, **11**, 6) failed to obtain the neutral chloropyrophosphate.

Chloropurpureocobalt Diphosphopentamolybdate. — The acid salt, $Cl_2.(Co_2 10NH_3)(5MoO_3.2PO_4H)$ and the neutral ammonium salt, $Cl_2(Co_2 10NH_3)(5MoO_3.2PO_4NH_4)$ have both been prepared; the former as a rose-red crystalline powder, by precipitating a cold solution of the purpureochloride with a solution of molybdic acid in excess of phosphoric acid; and the latter by using a solution of the corresponding ammonium phosphomolybdate as precipitant.

In a note appended to his paper the author states that he has prepared a few *chloropurpureo-chromium salts, e.g.*, $Cl_2(Cr_2.10NH_3)Cl_4$, &c., and has obtained results indicating the existence of a series of *Luteo-* and also of *Roseo-chromium* compounds. M. M. P. M.

Double Salts of Cuprous Thiosulphate. By F. Kesel (*Deut. Chem. Ges. Ber.*, **11**, 1581—1586).—The author has shown in a previous paper (this *Journal*, 1878, 113) that the composition of the yellow salt which is formed by mixing together solutions of cupric sulphate and sodium thiosulphate, is dependent upon the temperature employed. At 10° it has a composition quite different from that of the salt which had been prepared at −10°; and on decreasing the temperature still further, light yellow crystals separate, which dissolve to a colourless solution in ice-cold water. It appears, therefore, that at a temperature under −10°, soluble double salts only are formed, and these most probably contain a larger proportion of sodium thiosulphate.

Siewert's formula for the yellow salt, $Na_2S_2O_3.Cu_2S_2O_3.CuS$, is definitely confirmed. This salt can be easily prepared if the solutions mixed at the ordinary temperatures be kept at 0° whilst the salt is separating. The proportion of cupric sulphate and sodium thiosulphate required to form the compound, $Na_2S_2O_3.Cu_2S_2O_3.CuS$, was found by several methods of examination to be as $2S_2O_3Na_2.CuSO_4$, and not in the proportion of $5S_2O_3Na_2.3CuSO_4$, as stated by Siewert.

The yellow salt, when anhydrous, dissolves in concentrated hydrochloric acid to a deep brown colour, whereas the freshly prepared and moist salt is converted into a white insoluble powder, as described in the author's previous paper. This marked distinction between the two compounds is ascribed to their difference in hydration. Alcohol precipitates a light brown powder from the brown acid solution; the supernatant liquid contains cupric chloride. The analysis of the brown powder (dried over sulphuric acid) showed it to be a thiosulphate, and gave numbers corresponding with the formula,

$$[(S_2O_3)_2Cu_2Na_2](CuS)_2.$$ A. J. C.

Decomposition of Lead Sulphate by Sodium Chloride. By F. Matthey (*Arch. Pharm.* [3], **13**, 233—241).—A mixture of lead oxide, lead sulphate, and sodium chloride is found to react, producing lead chloride, the amount of lead chloride formed being in direct proportion to the lead oxide present, but in an inverse proportion to the sodium chloride; the whole of the lead sulphate may, however, be removed from the mixture by repeated treatments with sodium

chloride. Owing to the lengthened exposure of the above mixture to the air, carbon dioxide was absorbed, and this caused the formation of a chlorocarbonate, $Pb_2Cl_2CO_3$. E. W. P.

Mechanical Purification of Mercury. By G. Vulpius (*Arch. Pharm.* [3], **13**, 231).—Mercury is freed from dirt by causing it to pass through a thick filter, in which several holes have been pierced by a needle. E. W. P.

Atomic Weight of Iridium.—By C. Seubert (*Deut. Chem. Ges. Ber.*, **11**, 1767—1772).—The author has determined the atomic weight of iridium (1), by estimating the amount of iridium in iridium ammonium chloride; and (2) by estimating the iridium and the potassium chloride in iridium potassium chloride. The number 192·744 was obtained as the mean of 15 experiments. W. C. W.

Double Salts of Dyad Iridium. By C. Seubert (*Deut. Chem. Ges. Ber.*, **11**, 1761—1767).—In separating iridium from rhodium by means of hydrogen sodium sulphite, by Bunsen's process, the following double salts were obtained, viz., $IrSO_3.3Na_2SO_3 + 10H_2O$, cream-coloured scales; $IrH_2(SO_3)_2.3Na_2SO_3 + 4H_2O$, broad white needles; and $IrH_2(SO_3)_2.3Na_2SO_3 + 10H_2O$, in thin white needles. These salts have an acid reaction; they are almost insoluble in cold water, and are decomposed by hot water and by acids.

When aqueous sulphurous acid is heated with iridium-ammonium chloride to 70°, an olive-green solution is formed (reddish-brown by transmitted light), which deposits a green crystalline powder on evaporation. From the aqueous solution of this compound dark green needles (brown by transmitted light) separate out, having the composition, $Ir_2Cl_6.6NH_4Cl + 3H_2O$. On cooling down the concentrated mother-liquor to a low temperature, an acid having the composition, $Ir.Cl_2.SO_3H_2.4NH_4Cl$, is obtained in orange-coloured needles. It is very soluble in water, but is not deliquescent. It decomposes alkaline carbonates, forming salts. Its ammonium salt, $IrCl_2.SO_3(NH_4)_2.2NH_4Cl + 4H_2O$, crystallises in rhombic plates, and the potassium salt, $IrCl_2SO_3K_2.2NH_4Cl + 4H_2O$, forms small red crystalline scales. W. C. W.

Mineralogical Chemistry.

Mineral Waters of the Couban, in the Caucasus. By E. Wroblewsky (*Bull. Soc. Chim.* [2], **30**, 436).—These waters are remarkable for the quantities of bromine, iodine, and lithium they contain. 1,000 parts left 15·75408 parts of residue, containing NaCl, 14·05290; $MgBr_2$, 0·07621; MgI_2, 0·03054; LiCl, 0·01433. L. T. O'S.

Mineral Waters of Buda-Pesth. By M. Ballo (*Deut. Chem. Ges. Ber.*, **11**, 1900—1904).—This paper contains complete analyses of

certain thermal and bitter waters of Buda-Pesth, which are merely of local interest. C. F. C.

The Mineral Springs of Passugg, Solis, and Tiefenkasten, in the Grisons, Switzerland. By A. v. Planta-Reichenau (*Deut. Chem. Ges. Ber.*, **11**, 1793—1799).—The author gives the results of his analyses of the following mineral waters:—I. The alkaline Ulricus well. II. The chalybeate Theophilus spring, both at Passugg, near Coire. III. The Donatus well (containing iodine) at Solis. IV. The saline chalybeate, St. Peter's well, at Tiefenkasten.

	I.	II.	III.	IV.
Temperature of the spring	8·1	7·5	8·1	10°
Specific gravity	1·007 at 11°.	1·0036 at 14°.	1·0045 at 14°.	1·00453 at 11°.
10,000 parts of the water contain:—				
Total solids	60·376	29·178	49·952	46·270
K_2SO_4	1·568	1·340	0·702	1·150
Na_2SO_4	0·862	1·970	20·400	22·862
$NaNO_3$	0·04	0·007	0·067	0·023
$NaBoO_2$	0·067	—	—	—
LiCl	0·06	—	—	—
NaCl	8·371	2·221	12·037	5·876
NaBr	0·054	—	0·024	—
NaI	0·008	0·001	0·013	—
Na_2CO_3	37·946	13·513	2·089	—
$(NH_4)_2CO_3$	0·147	0·004	0·003	0·012
$CaCO_3$	71·25	7·057	7·750	11·839
$MgCO_3$	3·786	2·843	2·509	—
$SrCO_3$	—	0·005	0·004	0·003
$FeCO_3$	0·078	0·101	0·137	0·212
SiO_2	0·190	0·114	0·149	0·378
$AlPO_4$	0·074	—	0·068	—
Free CO_2	18·382	21·565	7·361	11·506
Bromine	—	trace	—	trace

I also contains a trace of barium; II contains 0·005 $MnCO_3$; III, a trace of boric acid; and IV, $MgSO_4$, 1·150; $CaSO_4$, 2·145; and $Al_2(CO_3)_3$, 0·013 parts in 10,000. W. C. W.

Organic Chemistry.

Action of Alcoholic Potash on Bromoform.—By H. Long (*Liebig's Annalen*, **194**, 23—27).—Alcoholic potash was mixed with bromoform in a flask holding about a quarter of a litre, and the gases liberated from the mixture were passed first through a long **U**-tube cooled by a refrigerating mixture, to free them from bromoform

carried over, and then through three very small wash-bottles, the first filled with alcohol, and the other two with water. The gas was collected in small tubes over mercury, and submitted to analysis in the eudiometer.

In order to determine the influence of the quantity of the potash, solutions of four different degrees of concentration were employed. The result was that the author realised in all cases the proportions 1 : 3 of the gases, ethylene and carbon monoxide, which were evolved, and so confirmed the previous results obtained by Hermann,—and at the same time the remarkable fact that ethylene and carbon monoxide, although they arise from two different materials, alcohol and bromoform, yet stand to one another in the simple volumetric relations of 1 : 3.

The author is inclined to regard this process as a pure volumetric one, whilst he presumes, that of the three bodies acting on one another, two first unite to form a compound, which is then decomposed by the third. W. S.

Preparation of Ethyl Bromide. (*Dingl. polyt. J.*, **229**, 284—288).—In this article an account is given of the method employed on the large scale for obtaining ethyl bromide from potassium bromide, by acting on it with a mixture of sulphuric acid and alcohol. A charge of 50 kilos. of commercial potassium bromide, containing about 95 p. c. KBr, is heated in a boiler with 50 kilos. of alcohol, 100 kilos. of sulphuric acid (sp. gr. 183), and 30 kilos. of water. The course of the reaction is ascertained by means of a thermometer ; it begins at 90°, but the temperature must finally be raised to 125—130°. The vapours are condensed by a worm, and the ethyl bromide collected under water. The yield is the theoretical ; some alcohol and ether pass over with the bromide.

The above reaction may also be used for obtaining the value of a sample of bromide, the operation described above being conducted on the small scale ; the ethyl bromide collected under water, its volume measured, and its weight determined. x = volume of ethyl bromide ; y = volume of ether present ; v = measured volume of the product ; P = the weight of the product.

$$(1.)\ x + y = v.$$
$$(2.)\ 1{\cdot}4x + 0{\cdot}74y = v \times \text{sp. gr.} = \text{P}.$$
$$\therefore x = \frac{\text{P} - 0{\cdot}74y}{0{\cdot}66}$$

and $x \times 1{\cdot}4$ is the amount of ethyl bromide obtained from the weight of potassium bromide taken. P. P. B.

Isomerism in the Propyl or Tri-carbon Series. By Reboul (*Ann. Chim. Phys.* [5], **14**, 453—511).—The author has endeavoured in this memoir to present a comprehensive sketch of the various isomerides belonging to the tri-carbon series, including therein not only the haloïd substitution-derivatives of propane, but also the derivatives of the symmetrical propyl-glycol, and symmetrical pyrotartaric acid (glutaric acid).

Dichloropropanes.—*α-Dichloropropane*, $CH_3.CCl_2.CH_3$ is generally prepared by the action of phosphoric chloride on acetone, but has also been obtained by the author by the direct combination of HCl with allylene. It boils at 69—70°, and gives by the action of alcoholic potash the chloropropylene, $CH_2{=}CCl.CH_3$, boiling at 23—25°. The identity of the two products is further shown by the fact that they both yield the same di-benzoic compound, $CH_3.C(C_7H_5O_2)_2.CH_3$, when treated with silver benzoate.

β-Dichloropropane, $CH_3.CH_2.CHCl_2$, is made by the action of phosphoric chloride on propaldehyde, but a good deal of the chloropropylene, $CH_3.CH{=}CHCl$, is formed at the same time. Its boiling-point is 85—87°, and its density 1·143 at 10°. With alcoholic potash it furnishes the chloropropylene before mentioned, which at a higher temperature, 130°, under the influence of the same reagent, is converted into allylene, $CH_3.C{\equiv}CH$. It yields no diacetic compound by treatment with potassium acetate.

γ-Dichloropropane, $CH_3.CHCl.CH_2Cl$. The action of HCl on allyl chloride, $CH_2{=}CH.CH_2Cl$, does not yield, like HBr on the bromide, a mixture of the two chloro-compounds, but only the γ-dichloropropane. Allyl chloride is heated for 18 hours at 100°, with very concentrated HCl; the superior layer, which is of a violet-black colour, is separated and submitted to fractional distillation. The greater part of it consists of ordinary or γ-dichloropropane, boiling at 96—97°. It is noticeable that the difference, 22°, between the boiling-points of the symmetrical and unsymmetrical dichloropropanes is the same as the difference between those of the corresponding dibromides.

δ-Dichloropropane, $CH_2Cl.CH_2.CH_2Cl$, can be obtained from the corresponding dibromide by heating it with mercury chloride in sealed tubes at 180° for several hours, or by treating the symmetrical propyl glycol with HCl. In the latter case, monochlorhydrin of glycol, $CH_2(OH).CH_2.CH_2Cl$, is formed at the same time; they are, however, easily separated, since the dichloropropane boils at 119°, and the monochlorhydrin at 162°. Its density is 1·201 at 15°.

Chloropropylenes.—*α-Chloropropylene*, $CH_3.CCl{=}CH_2$, results from the abstraction of HCl from α-dichloropropane by means of alcoholic potash. Its boiling point is 25°.

β-Chloropropylene, $CH_3.CH{=}CHCl$, is prepared in the same manner from β-dichloropropane, by heating it for 4 or 5 hours under pressure with excess of the reagent; a small quantity of the dichloropropane escapes action, and a little allylene is formed. The chloropropylene is a very mobile liquid, lighter than water, boiling at 35—36°.

α-Chloropropylene unites with HBr, furnishing only *one* chlorobromide, $CH_3.CClBr.CH_3$, boiling at 93°; it likewise fixes Br_2, and gives the dibromide, $CH_3.CClBr.CH_2Br$, boiling at 169—170°.

β-Chloropropylene, in uniting with HBr, gives the chlorobromide, $CH_3.CH_2.CHClBr$, boiling at about 110°, mixed with a little $CH_3.CHBr.CH_2Cl$, which passes over towards 121°. When cooled to −15°, it gives with bromine the dibromide, $CH_3.CHBr.CHClBr$, boiling at 177—177·5°.

While the two dichloropropanes α and β break up under the action of potash, yielding *one* chloropropylene respectively, ordinary or γ-dichloro-

propane in which the two atoms of chlorine (or bromine) belong to adjacent carbon groups, gives a mixture of the chloropropylenes α and β, the former predominating. A mixture of chloropropylenes with Friedel and Silva's chlorobromide, $CH_3.CHCl.CH_2Br$, was also produced, which is sufficient to account for the anomalous results obtained by these chemists.

γ-Chloropropylene, $CH_2{=}CH.CH_2Cl$, is identical with allyl bromide.

Dibromopropanes. *α-Dibromopropane*, $CH_3.CBr_2.CH_3$.—It appears to be almost impossible to make this body by the action of PBr_5 on acetone, but it can be easily prepared by the direct addition of HBr to allylene, or to α-bromopropylene. If HBr of not less than 66° B. is added to allylene enclosed in a vessel over mercury, the absorption of the gas is complete in about 4 or 6 hours at 0°, and by replacing the gas according as it is absorbed, very considerable quantities of the dibromide can be obtained. The product is contaminated, however, with a little α-bromopropylene, from which it can be readily separated by a few distillations.

The action of HBr on α-bromopropylene also gives a very pure product; but it is more convenient to work upon the mixture of propylenes given by ordinary dibromopropane in the manner described under β-bromopropylene. Its density at 10° is 1·875, and its boiling point 114—114·5° under 740 mm.

β-Dibromopropane, $CH_3.CH_2.CHBr_2$.—Although the existence of this bromide can be shown independently of theoretical considerations, it has never been satisfactorily isolated. The action of PBr_5 on propyl aldehyde closely resembles the corresponding action on acetone; torrents of HBr are evolved from the commencement of the operation, but as soon as distillation is proceeded with, the liquid turns black, evolves more HBr, and leaves finally an abundant carbonaceous residue. From the distillate, after the removal of phosphorus oxybromide, a little β-bromopropylene can be separated, but no β-dibromopropane can be obtained. The operation is not more successful when the oxybromide is removed by means of water, without previous distillation.

By combining HBr with the bromopropylene, $CH_3.CH{=}CHBr$, in the cold, the two dibromides are simultaneously produced. Unfortunately, fractional distillation fails to separate them, on account of the proximity of their boiling points. On submitting the washed and dried liquid to distillation, the boiling point quickly rises to 135°, and the whole passes over between 135° and 143°, the greater portion distilling between 139° and 140°. The boiling point of the β-compound should be 131—133°, while that of the ordinary or γ-dibromopropane is 143°. The same result obtains if the combination of HBr with the bromopropylene takes place at 100°.

δ-Dibromopropane, $CH_2Br.CH_2.CH_2Br$.—The action of HBr on allyl bromide forms simultaneously two isomerides, the normal or δ-dibromopropane and the ordinary or γ-dibromopropane. The relative proportion of the two bromides varies with the concentration of the acid, with the temperature, and with the duration of the action. The

best method of operating is as follows:—One volume of allyl bromide and $3\frac{1}{2}$ vols. of fuming HBr are heated under pressure at 100° for 15 to 20 minutes, and the dark coloured oily product subsequently washed and distilled. A good deal of unaltered allyl bromide passes over first, and then the thermometer rapidly rises to 140—145°. The distillate is collected from this point up to 175°. On submitting this portion to repeated fractional distillation, the δ-dibromopropane can be easily separated, boiling at 164—165°, the yield being a little more than one-half of the allyl bromide operated on. If the solution of HBr is not saturated, or if the time of heating be prolonged, a largely increased yield of ordinary dibromide is obtained at the expense of the normal or δ-compound; even with a strongly fuming acid, it is not advisable to heat the mixture longer than 20 minutes, for no increased yield of the desired product is obtained. Its density is 1·9839 at 13·5°. It is much more susceptible of double decomposition than the ordinary dibromide, forming with great facility the compound ethers of the corresponding glycol.

Bromopropylenes.—*α-Bromopropylene*, $CH_3.CBr{=}CH_2$.—The best method of preparing this compound is to heat α-dibromopropane for five or six hours at 100° with sodium ethylate containing exactly the quantity of sodium necessary to remove one-half of the bromine. The product, when distilled and washed with water, gives, after several rectifications, the α-bromopropylene in a state of purity.

It is a mobile liquid, boiling at 47—48° under a pressure of 742 mm. Its density is 1·39 at 9°, or 1·362 at 20°. By its union with HBr it gives only *one* compound, namely, the dibromopropane from which it was originally prepared, boiling at 114·5°; with bromine it yields the tribromide $CH_3.CBr_2.CH_2Br$, boiling at 190—191°; sp. gr. 2·33 at 12°.

β-Bromopropylene, $CH_3.CH{=}CHBr$.—The author has most satisfactorily proved by numerous conclusive reactions that ordinary bromopropylene derived from the ordinary dibromide (γ) by loss of HBr is a mixture of the two bromo-derivatives, $CH_3.CBr{=}CH_2$ and $CH_3.CH{=}CHBr$. Unfortunately, on account of the proximity of their boiling points, they cannot be separated by fractional distillation. The mixture distils between 50° and 60°. Operating on 250 grams of this mixture, a small proportion was obtained by means of five or six fractionations (*a*) (49—52°), a very considerable portion (*b*) (52—57°), and a smaller quantity (*c*) (57—60°). The first portion was very rich in α-bromopropylene, for when heated with HBr it was converted in the cold into a dibromide (α) boiling almost constantly at 114°, and the latter portion (*c*) was equally rich in β-bromopropylene, since it yielded under the same treatment very little of the α-dibromide. The separation, however, was successfully effected by taking advantage of the double fact that HBr attaches itself much more rapidly to α-bromopropylene than to its isomeride (β), and that the combination formed with the first compound is the more stable of the two. By thus sacrificing a portion of the β-bromopropylene, the whole of the first compound (α) may be completely removed. For example, one volume of ordinary monobromopropylene was treated at 100° with 4 to 5 vols. of saturated HBr for five or six hours, and the product washed

and fractionated. The portion which came over first from 59·5° to 60° consisted wholly of the β-bromopropylene without any trace of its isomeride, for when acted on further by HBr it gave a mixture of the two dibromopropanes, β and γ, unaccompanied by the α-compound. Its density was 1·428 at 19·5°.

The mixture of the three bromides resulting from the addition of HBr to ordinary bromopropylene may be distilled, and the portion boiling under 135° collected and decomposed by rapid distillation with concentrated alcoholic potash. Under these conditions the two isomerides of α-dibromopropane are completely destroyed, while the latter is only partially acted on. By fractionating the distillate, the α-dibromo compound boiling at 114° may be readily separated. This, when broken up by potash or sodium ethylate, furnishes pure α-bromopropylene, boiling at 47—48°.

By treating β-bromopropylene with bromine in the cold, the tribromopropane, $CH_3.CHBr.CHBr_2$, is obtained. It boils at 200—201°, or 10° higher than the isomeride furnished by α-bromopropylene. Its density is 2·356 at 18°.

Chlorobromopropanes.—Five chlorobromopropanes ought theoretically to exist, α, β, and δ, analogous to the chlorides and bromides α, β, and δ, and two others, γ and γ′, corresponding to the chloride γ.

α-Chlorobromopropane, $CH_3.CClBr.CH_3$, is very easily obtained by the action in the cold of excess of concentrated HBr on α-chloropropylene. Its isomeride, $CH_3.CCl.CH_2Br$, is not produced in the cold, but only on heating. It boils at 93—93·5°, and its density is 1·474 at 21°.

The bromiodide may be prepared in a similar manner by the action of HI on α-bromopropylene. On distillation nearly the whole product passes over at 147°, slightly coloured by free iodine. Its density is 2·2 at 11°.

β-Chlorobromopropane, $CH_3.CH_2.CHClBr$, results from the addition of HBr to β-chloropropylene without application of heat. It is generally accompanied by a small quantity of its isomeride, $CH_3.CHBr.CH_2Cl$, but the latter is easily separable on distillation. Its density is 1·59 at 20°, and its boiling point 110—112°.

γ-Chlorobromopropanes, $CH_3.CHCl.CH_2Br$ and γ′ $CH_3.CHBr.CH_2Cl$. —By maintaining for some hours at the boiling point a mixture of ordinary dibromopropane and mercuric chloride in an apparatus fitted with an inverted condenser, Friedel and Silva obtained a chlorobromide boiling at 119—121°, which they considered to be the compound $CH_3.CHCl.CH_2Br$, because when decomposed with alcoholic potash it yielded α-chloropropane boiling at 25—30°. The author points out that the chlorobromide made in this manner is in reality a mixture of the two isomerides, and that the supposed α-chloropropylene contains a certain proportion of its isomeride (β). By treating the mixed chloropropylenes with HBr in the cold, it is possible to remove the whole of the α-compound as $CH_3.CClBr.CH_3$ boiling at 93°, without acting on the β-compound, so that the presence of β-chloropropylene in the mixture is by this reaction placed beyond doubt, indeed the latter compound can be obtained from this source

in a state of great purity if the last traces of its isomeride (α) be removed by a second treatment with hydrobromic acid.

δ-Chlorobromopropane, $CH_2Cl.CH_2.CH_2Br$.—Allyl chloride is heated for seven or eight hours at 100° in a closed vessel, with a concentrated solution of HBr, then washed, dried, and fractionated. When quite free from allyl chloride, it distils at 140—142°, and has a density of 1·63 at 8°; it is, however, very difficult to free it entirely from a trace of the chlorobromide, $CH_2Cl.CHBr.CH_3$, and of δ-dibromopropane, which are formed at the same time, although in small quantity. By the action of sodium on the isomeric bromopropanes, one and the same propylene is always formed, namely, $CH_3.CH{=}CH_2$, therefore the four isomeric propylenes corresponding to the four dibromides do not exist.

When in the dichloro- and dibromo-propanes the two chlorine or bromine atoms are attached to the same carbon atoms, they cannot be substituted by acid radicles; when treated with silver acetate they lose HCl or HBr, and give monochloro- or monobromo-propylene. In the case of α-dibromopropane, it is possible to obtain a dibenzoic compound, but water resolves it into acetone and benzoic acid. The glycols corresponding to the same compounds do not exist, or if they exist are eminently unstable, being easily resolved into water and acetone or propyl aldehyde. It is possible, however, to attach two COOH groups to the same carbon atom, and the acids, dimethyl-malonic and ethyl-malonic, resulting from such substitutions have been known for some time.

Second Part.—*Symmetrical Propyl Glycol*, $CH_2(OH).CH_2.CH_2(OH)$. —This glycol is easily prepared by converting the symmetrical δ-dibromopropane into the corresponding diacetate, and then saponifying the latter with baryta. 170 grams of the dibromide are boiled with 180 grams of potassium acetate and 350 grams of alcohol in a flask fitted with an inverted condenser from 12 to 15 hours (or the mixture may be heated under pressure at 100° for 3 or 4 hours), the liquid is decanted from the potassium bromide, the latter washed with absolute alcohol, and the whole of the alcohol distilled off in a water-bath. The impure diacetate may be decanted from the second deposit of bromide, and distilled in an oil-bath, those portions being collected which come over between 200 and 215°.

This portion on rectification distils almost entirely between 208° and 211°, and consists of the nearly pure diacetate, weighing about 111 grams, being very nearly the theoretical yield.

The diacetate is best saponified by mixing it with water, and adding crystals of barium hydrate in small successive portions, the flask containing the liquid being kept at 100°. In order to saponify the 111 grams of acetate before-mentioned, 216 grams of crystallised hydrate were necessary. The slight excess of baryta is precipitated by a current of carbon dioxide, the liquid boiled for a few minutes, and then allowed to stand for some hours. The liquid, decanted from the barium acetate which has crystallised, is concentrated on a water-bath, then mixed with the alcoholic washings from the barium salt, and allowed to cool a second time, in order that a further deposit of

barium acetate may be obtained. On finally distilling in an oil-bath, the thermometer quickly rises to 210°, as soon as the alcohol has passed over, and the whole distils between 210 and 230°. The weight of the redistilled product was 42 to 43 grams.

Symmetrical propyl glycol is a thick colourless liquid, sweet to the taste, and soluble in water and alcohol in all proportions; its density is 1·053 at 19°, and its boiling-point is 255—216° (corrected by 4°).

Chlorhydrins.—The glycol is saturated with hydrochloric acid, and heated for five or six hours at 100° in a closed tube. The tube having been opened, the contents are resaturated with acid, and again heated for about the same time. On separating the oily layer which has formed, and submitting it to fractional distillation, it will be found to boil at 119°, and to be identical with the symmetrical dichloropropane obtained as before mentioned.

The liquid from which the dichlorhydrin has been separated is resolved on distillation into water and the monochlorhydrin boiling at 160—162°, very little of the propylglycol escaping etherification.

The two chlorhydrins are produced at the same time, and generally in about equal proportions; the relative quantity of the monochlorhydrin may be increased by using a deficiency of hydrochloric acid, but the formation of the dichlorhydrin cannot be altogether avoided; there is, however, a great disadvantage in diminishing the proportion of hydrochloric acid used, as under such circumstances a great deal of the glycol escapes action. The density of the monochlorhydrin is 1·132 at 17°.

Symmetrical Propylene Oxide, $O<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2$.—Solid potash in fine powder is made to act upon the monochlorhydrin; on gently warming the mixture, the action soon starts and propylene oxide distils over. The distillate is afterwards digested with dry potassium carbonate, and rectified in a water-bath. It is a colourless, very mobile liquid, boiling at about 50°; it possesses a penetrating odour, is soluble in water in all proportions, and combines energetically with bromine. Unfortunately, on account of its tendency to become polymerised, it is difficult to prepare in any quantity.

A mixture of polyoxypropylenes may be separated by adding water to the residues from which the propylene oxide has been distilled; an abundant oily deposit takes place, which, when taken up and separated by ether, gives, on distillation, a small quantity of a liquid boiling between 160 and 170°, but scarcely anything afterwards, even up to 320°. The larger portion of the product (which does not appear to have been distilled) gives the same analytical results as the portion boiling below 160°, and may be represented by the formula $n(C_3H_6O)$.

The compound ethers of propyl glycol are readily obtainable by heating the dibromide with the potassium or silver salt of the required acid, in presence of alcohol or ether. In this manner the diacetate, divalerate, and dibenzoate have been prepared. The diacetate boils at 209—210°, and has a specific gravity of 1·07 at 19°; the divalerate at 269—270°, density 0·98 at 12°; the dibenzoate, which is a beautiful crystalline body, melts at 53°.

THIRD PART.—*Symmetrical Pyrotartaric Acid*, $COOH.(CH_2)_3.COOH$.

One molecule of the symmetrical dibromide is heated with two molecules of potassium cyanide dissolved in alcohol, in a flask with inverted condenser for some hours. The product is decanted from the potassium bromide, and distilled until the thermometer has risen to 140—150°. To the residue, which consists of impure dicyanide, are added, after cooling, $2\frac{1}{2}$ volumes of hydrochloric acid. The mixture becomes heated, and sal-ammoniac separates; to complete the reaction however, it is advisable to heat the whole under pressure at 100° for one hour. The solid mass is heated in a water-bath to get rid of excess of hydrochloric acid, then dissolved in strong alcohol to remove ammonium chloride, and the alcoholic solution is distilled, with addition of a known weight of barium hydrate, to avoid etherification of the pyrotartaric acid. The barium pyrotartrate is dissolved in water, decolorized with animal charcoal, decomposed by dilute sulphuric acid, and the pyrotartaric acid crystallised.

Operating on 200 grms. of ô-dibromopropane in the manner above described, 106—107 grms. of pure crystallised acid were obtained, instead of the theoretical yield, 130 grms. Its melting point is 9·65°; on further heating it loses a little water, but distils without decomposition at 299° (corr.), 291° (uncorr.); however its melting point is a little lowered, being now 94—95·5°. It is very soluble in water, alcohol, and ether, one part of the acid dissolving in 1·2 parts of water at 14°.

Pyrotartaric Chloride.—$COCl(CH_2)_3.COCl$ is obtained by the action of 2 molecules of PCl_5 on 1 molecule of the acid. It is a heavy liquid having an irritating odour; it boils at 216—218°, with sensible decomposition. By the action of water it is converted into hydrochloric and pyrotartaric acids.

Diethyl Pyrotartrate.—This compound ether may be prepared in the usual manner, by dissolving the acid in absolute alcohol, and saturating with hydrochloric acid gas. On distilling the product, that portion is collected which comes over between 240 and 260—265°; it consists chiefly of pyrotartaric ether, and acid which has not been etherified; the latter is removed by digestion with potassium carbonate, and the ethereal liquid redistilled. The pure ethyl salt is a colourless liquid of disagreeable odour, boiling without decomposition at 236·5—237°; its density is 1·025 at 21°.

Thirteen salts of pyrotartaric acid have been prepared and examined by the author; the neutral and acid salts of potassium, sodium, and ammonium, and the salts of barium, calcium, magnesium, zinc, copper, and silver. It is unnecessary to describe them in detail, since they present no characteristics requiring special notice. Their composition may be represented by the formulæ, $R_2'C_5H_6O_4$ and $R''C_5H_6O_4$.

J. W.

Isopropylacetylene. By F. Flawitzky and P. Kriloff (*Deut. Chem. Ges. Ber.*, **11**, 1939—1940).—The authors supplement their previous communications (*Ber.* **10**, 1102 and 2240), by the following. Isopropylacetylene boils at 28—29° (751 m.m.), its sp. gr. at 0° is 0·6854. The silver compound, C_5H_7Ag, they find to be specifically heavier and not lighter than water, as stated by Eltekoff (*Ber.*, **10**, 707). It is soluble in absolute alcohol, and is partially

precipitated from this solution by ether: the remainder crystallises in small prisms on evaporation of the ether-alcoholic solution. By the action of sulphuric acid on isopropylacetylene, in addition to methylisopropyl ketone (*Ber.*, **10**, 2240), other products are formed, boiling between 1000 and 3200°, which appear to result from the condensation of the ketone. C. F. C.

Derivatives of Brain Cholesterin. By W. Walitzky (*Deut. Chem. Ges. Ber.*, **11**, 1937—1938).—By heating together aniline and cholesterin chloride in sealed tubes at 180°, cholesterilaniline, $C_{25}H_{41}.(C_6H_5)NH$ is formed. This base crystallises from its solution in carbon bisulphide in large rectangular plates (m.p. 18°); it forms crystalline salts with the mineral acids. The corresponding toluidine compound may be similarly prepared. It is precipitated in small plates from its ethereal solution on adding alcohol; it crystallises on evaporation in large plates (m.p. 172°). Of its salts, the nitrate is the most stable; the hydrochloride and sulphate are resolved by boiling water or alcohol into acid and base. Naphthylamine yields a similar compound, melting at 202°. All the above bases are precipitated by mineral acids from their ethereal solutions. C. F. C.

Some Neutral Oxidation-products of Cholesterin. By P. Latschinoff (*Deut. Chem. Ges. Ber.*, **11**, 1941—1943).—In addition to the cholesterin acids previously described, the author finds that certain neutral bodies are formed by the oxidation of the acetic solution of cholesterin by potassium permanganate. They are resinous, soluble in alcohol, and uncrystallisable; a portion is precipitated by alcoholic lead acetate, but it was found impossible to isolate the individual compounds; the filtrate from the precipitate yielded a body having approximately the composition of trioxycholesterin, and appeared also to hold in solution certain compound cholesterin ethers, *i.e.*, bodies which after boiling with alcoholic potash were largely dissolved by aqueous alkalis. More satisfactory results were obtained with cholesterin acetate and potassium permanganate. From the mixed product of this oxidation, ether dissolved a quantity of the diacetin of trioxycholesterin, $C_{29}H_{46}O_5$, the formation of which is explained by the equations: $C_{25}H_{41}(C_2H_3O_2) + O_2 = C_{25}H_{41}O_2(C_2H_3O_2)$ and $C_{25}H_{41}O_2(C_2H_3O_2) + C_2H_4O_2 = C_{25}H_{40}O.(C_2H_3O_2)_2 + H_2O$. This body is soluble in ether, benzene, alcohol, and other menstrua; it melts at 77°, and solidifies to a yellowish mass resembling colophony. Its composition was determined by combustion and by the quantitative investigation of its saponification. The trioxycholesterin which it yields on saponification, is a yellowish powder soluble in ether, benzene, and alcohol; it is not precipitated by lead acetate from its solution in the latter. It forms an emulsion with ammonia.

From the products of the oxidation of cholesterin by nitric acid diluted with glacial acetic acid, the author has isolated a body crystallising in pearly, yellowish-green plates, soluble with difficulty in ether, alcohol, and glacial acetic acid. It is easily decomposed by aqueous alkalis, yielding trioxycholesterin and a nitrite. It appears to be the nitrous ether of trioxycholesterin, and to be formed according to the equation: $C_{25}H_{42}O_3 + 3NO_2H = C_{25}H_{39}N_3O_6 + 3H_2O$. C. F. C.

Presence of Ethyl Alcohol in Coal Tar. By O. Witt (*Chem. Centr.*, 1878, 416).—Crude benzole from coal tar contains about two parts of ethyl alcohol per million; a fact which has hitherto been overlooked, probably on account of the very small quantity present.

M. M. P. M.

Preparation of Dipropylallylcarbinol. By A. and P. Saytzeff (*Deut. Chem. Ges. Ber.*, **11**, 1939).—The authors have prepared this new alcohol by the action of zinc on a mixture of allyl iodide and butyrone. It boils at 192°, is insoluble in water, but miscible with alcohol and ether in all proportions. Its sp. gr. at 0° is 0·8602; at 24°, 0·8427 (referred to water at 0°): its expansion co-efficient is 0·00086. The acetate boils at 210°; sp. gr. at 0° = 0·8903, at 21° = 0·8733 (referred to water at 0°); its expansion co-efficient 0·00092. With bromine, it forms an addition-product containing 2 at. bromine. On oxidation with chromic mixture, it yields butyrone, propionic acid, and butyric acid.

C. F. C.

Dehydration of Propylene Glycol. By F. Flawitzky (*Deut. Chem. Ges. Ber.*, **11**, 1940—1941).—The author has previously observed (*Ber.* **11**, 1256) that the dehydration of propylene glycol by sulphuric acid and zinc chloride, yields only propaldehyde and, probably, condensation-products of the same; on the other hand, Eltekoff, by heating this glycol with water at 180—190°, obtains acetone in addition (*Ber.*, **11**, 990), whilst Linnemann (*Annalen*, **192**, 61) finds that propaldehyde is the sole product of this reaction. The author believes Eltekoff to be in error on this point. He also denies the latter's interpretation of the action of water upon propylene bromide in presence of lead oxide, on the ground that, since propaldehyde and acetone are products of the reaction, there must result, in addition to the formation and dehydration of propylene glycols, a separation of hydrobromic acid from a portion of the propylene bromide, which is thereby converted into monobromopropylene, and it is this body that reacts with water, according to an observation of Linnemann's (*Annalen*, **161**, 16), to form acetone.

C. F. C.

Specific Rotatory Power of Cane Sugar. By B. Tollens (*Deut. Chem. Ges. Ber.*, **11**, 1800—1810).—The results, which the author recorded in his previous paper (*Ber.*, **10**, 1403), have been confirmed by the researches of Schmitz (*ibid.*, **10**, 1414), but since they differ from those obtained by Girard and de Luynes (*Compt. rend.*, **80**, 1355), and by Calderon (*ibid.*, **83**, 393), he has repeated his experiments and has verified the correctness of his former conclusions.

The mean of the present experiments, made with a 10 per cent. solution of sugar and a Wild's polaristrobometer, gives, as the value of a 10 D (rotatory power of a 10 per cent. solution), 66·475°; the former experiments gave 66·649°, whilst Schmitz obtained 65·527°. The mean of the author's numbers is 65·550°, when the sp. gr. is referred to water at 4°, or 66·473° referred to water at 17·5°. In tables of sugar polarisation, the rotatory power is taken as 64·417°: hence the normal weight, *i.e.*, the weight of sugar in 100 c.c. of the solution, will be slightly larger than the number in the tables.

W. C. W.

Lactoglucose and Galactose. By G. Foudlakowsky (*Bull. Soc. Chim.* [2], **30**, 433).—The author has obtained lactoglucose and galactose by the action of sulphuric acid on cane sugar (*Chem. Soc. J.*, 1877, **2**, 897). The former melts at 70—71°, but after drying at 100°, it melts at 132—135°, the latter melts at 118—120°, but after heating to 100°, it melts at 142—144°. They both reduce Fehling's solution. Galactose when treated with a solution of baryta in methyl alcohol yields the compound $[(C_6H_{11}O_6)_2Ba]_2BaO$. Both glucoses yield pentacetyl compounds, $C_6H_7(C_2H_3O)_5O_6$. That from galactose melts at 62—66°, and that from lactoglucose between 47 and 51°. They also yield compounds with sodium chloride. When oxidised with nitric acid, lactoglucose yields gluconic, saccharic, and tartaric acids, whilst galactose yields mucic acid. L. T. O'S.

Occurrence of Furfuraldehyde in Glacial Acetic Acid. By V. Meyer (*Deut. Chem. Ges. Ber.*, **11**, 1870).—A preparation of glacial acetic acid (99—100 p.c.) which had been observed by the author to give a deep red coloration with aniline (*Ber.*, **11**, 697), he finds to contain furfuraldehyde. The quantity was estimated by a colorimetric test, based upon this property, and found to be 0·108 gram furfurol in 1,000 c.c. C. F. C.

Decomposition of Ethylsulphates by Gaseous Hydrochloric Acid. By H. Köhler (*Deut. Chem. Ges. Ber.*, **11**, 1929—1932).—The equation of decomposition of potassium ethylsulphate by hydrochloric acid $KC_2H_5SO_4 + HCl = KHSO_4 + C_2H_5Cl$ is realised quantitatively, at 145°; probably at a temperature as low as 65—85°. The barium salt is completely decomposed at 65—80°, according to the equation $Ba(C_2H_5SO_4)_2 + 2HCl = BaSO_4 + H_2SO_4 + 2C_2H_5Cl$. C. F. C.

Action of Ammonium Sulphate on Barium Ethylsulphate. By H. Köhler (*Deut. Chem. Ges. Ber.*, **11**, 1926—1928).—The author finds that the *à priori* equation of the reaction of these bodies in presence of barium oxide, $Ba(C_2H_5SO_4)_2 + 2NH_4SO_4 + 2BaO = 2NH_2.C_2H_5 + 3BaSO_4 + 2H_2O$, is only very imperfectly realised. Thus from 200 grams of barium ethylsulphate subjected to dry distillation with these reagents, in quantity determined by the above equation, only 2 grams of ethylamine hydrochloride were obtained. The greater part appears to suffer decomposition according to the equation, $Ba(C_2H_5SO_4)_2 = BaSO_4 + (C_2H_5)_2SO_4$.

The formation of carbamines was also observed, indicating more radical decompositions. C. F. C.

Bromo-derivatives of Ethyl Acetate. By F. Kessel (*Deut. Chem. Ges. Ber.*, **11**, 1916—1926).—The author has investigated the decomposition of dibrominated ethyl acetate (obtained by the action of bromine upon ethylidene chloracetate, $CH_3.COO(CHCl.CH_3)$, by alcohol. The products of the reaction are monobrominated ethyl acetate, crotonaldehyde, acetyl, ethyl bromide and hydrobromic acid; their formation is explained by the equation:—

(1.) $CH_2Br.COO(CHBr.CH_3) + C_2H_5.OH = CH_2Br.COOC_2H_5 + CH_3.CHBr(OH)$.

(2.) $CH_3.CHBr(OH) = HBr + CH_3.OH$.

The acetyl resulting from the action of the aldehyde thus formed upon alcohol; crotonaldehyde from the dehydrating action of hydrobromic acid; ethyl bromide from the action of this acid upon alcohol.

The formation of $CH_2Br.COOC_2H_5$ (1) proving the presence of the CHBr.CO group, and the second bromine atom replacing the chlorine atom in the chloracetate from which it is obtained, the constitution of the dibrominated ethyl acetate is that represented by the formula: $CH_2Br.COO(CHBr.CH_3)$ (*Ber.*, **10**, 1994). By the further action of bromine upon the same, the *tri-* and *tetra*-brominated ethereal salts are obtained. They are oily fuming liquids, which are decomposed on boiling. Treated with water or alcohol, they yield aldehyde derivatives, and hence still retain the COH group.

The tetrabromide may be further brominated by heating it at 170° with the requisite weight of bromine. The pentabromide thus obtained differs essentially in its properties and reactions from the preceding compounds. It is a limpid liquid, which fumes slightly in the air and boils at 175—177°. It is decomposed by water, but no aldehyde derivatives are thereby formed, but mono- and di-bromacetic acids; the reaction may be represented by the equation: $C_4H_3Br_5O_2 + 2OH_2 = C_2H_3BrO_2 + C_2H_2Br_2O_2 + 2HBr$.

It is similarly decomposed by alcohol, with formation of ethyl monobrom- and dibrom-acetates thus: $C_4H_3Br_5O_2 + 2C_2H_5OH = C_4H_6Br_2O_2 + C_4H_7BrO_2 + 2HBr$.

From the formation of ethyl dibromethylacetate the presence of a $-CHBr_2$-group in the pentabromide may be inferred; a third bromine atom replaces the chlorine atom of the original chloracetate, $CH_3.COO(CHCl.CH_3)$, from which it is obtained; the absence of aldehyde derivatives from the product of its decomposition by water suggests a $a-O-\overset{|}{C}=Br_2$ group. Of the two possible formulæ embodying these inductions, the following is assigned to the pentabromide, $CHBr_2.CBr_2.O.CO.CH_2Br$, as the more probable by reason of the fact that by the further action of bromine at a high temperature, only one hydrogen atom is replaced. The hexbromide thus obtained boils, almost undecomposed, at 195—198°; it closely resembles the pentabromide. The author's view of the constitution of this series of bromides is expressed by the formula, $\begin{matrix}(3:4)Br_2HC & CH_2Br(2)\\ | & |\\ (1:5)Br_2C—O & —CO\end{matrix}$, in which the numerals indicate the order in which the hydrogen is displaced. C. F. C.

Thioglycollic and Thiodiglycollic Ethers. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 1897—1900).—The author continues (from **10**, 1243) his investigation of the action of hydrogen sulphide in presence of argentic oxide upon glyoxylic acid. The product is treated so as to obtain the resulting acids in the form of ethers. In this way thioglycollic and thiodiglycollic acids have been isolated and identified. C. F. C.

Action of Phosphorus Pentachloride on Ethyl Oxalate. By V. v. Richter (*Chem. Centr.*, 1878, 446).—Equal numbers of molecules

of the pentachloride and ethyl oxalate react energetically when heated, with production of ethyloxalic chloride, viz., $C_2O_2Cl.OC_2H_5$. This body boils at 131°, not at 140°, as stated by Henry. The further action of phosphorus pentachloride on this chloride gave a product which, on treatment with water, yielded ethyl trichloracetate, $CCl_3.COOC_2H_5$: whether oxalyl chloride, $C_2O_2Cl_2$, is simultaneously produced is not yet determined.

The action of phosphorus pentabromide on ethyl oxalate is analogous to that of the chloride, the product being ethyl-oxalic bromide, $C_2O_2Br.OC_2H_5$: it boils at about 150°. M. M. P. M.

Hydroxylation by Direct Oxidation. By R. Meyer (*Deut. Chem. Ges. Ber.*, **11**, 1787—1790).—When an alkaline solution of cumic or of isobutyric acid is oxidised by potassium permanganate, an atom of hydrogen is replaced by hydroxyl, oxypropylbenzoic or oxyisobutyric acid being formed. This conversion of hydrogen into hydroxyl by oxidation appears to take place only when the formation of hydroxyl gives rise to a tertiary compound. W. C. W.

Isobutylformic Acid (Inactive Valeric Acid). By E. Schmidt and R. Sachtleben (*Liebig's Annalen*, **193** 87—114).—The potassium salt of this acid was prepared in large quantity by a slight modification of Erlenmeyer and Hell's method (*Annalen*, **160**, 264), in which the isobutyl cyanide is decomposed by alcoholic potash. The free acid boils at 175° (uncor.) under a pressure of 754·8 mm. Sp. gr. 0·93087 at 17·4. It is optically inactive. Its salts are partially converted into basic compounds on keeping: their aqueous solutions have a slightly acid reaction. The salts of the alkaline and alkaline earths are easily soluble in water, but those of the heavy metals are difficultly soluble. The latter are peculiar in that they are generally more soluble in cold than in hot water.

The *calcium salt* $(C_5H_9O_2)_2Ca + 3H_2O$, is more soluble than that of ordinary valeric acid, and is not so prone to form basic salts.

The *manganese salt*, $(C_5H_9O_2)_2Mn + 2H_2O$, the *zinc salt*, $(C_5H_9O_2)_2Zn + 2H_2O$, and the *copper salt*, $(C_5H_9O_2)_2Cu$, are more soluble in cold than in hot water.

Quinine isobutylformate, $C_{20}H_{24}N_2O_2.C_5H_{10}O_2$, closely resembles the ordinary valerate.

Methyl isobutylformate, $C_5H_9O_2.CH_3$, is a colourless liquid with a pleasant fruity odour (b. p. 117° at 763·8 mm.). Sp. gr. at 17° = 0·885465.

Isobutylformamide, $C_5H_9O.NH_2$, is prepared by heating the methyl salt with a mixture of aqueous and alcoholic ammonia for 5 hours at 120° in sealed tubes, and evaporating the product over sulphuric acid. It crystallises in silky plates (m. p. 135°), which are easily soluble in water and alcohol, and can be sublimed.

Isobutylformanilide, $C_5H_9O.NH(C_6H_5)$, is obtained by boiling equal molecular weights of the acid and aniline together for two days. It is sparingly soluble in hot water, but easily in alcohol or ether. It sublimes on heating, and volatilises in a current of steam (m. p. 100°).

Bromisobutylformic acid seems to be formed when isobutylformic acid is heated with bromine at 140°, but it could not be obtained in a pure state.

Amido-isobutylformic Acid (*Isopropylglycocoll*), $NH_2.C_4H_8.COOH$.—To prepare this compound, bromisobutylformic acid was heated with 4 vols. of concentrated ammonia in sealed tubes for 6 hours at 130°: after removal of the ammonia by evaporation, the residue was digested with lead hydroxide until it ceased to smell of ammonia, the precipitated lead bromide was filtered off, and the lead in solution removed by sulphuretted hydrogen; the filtrate, on evaporation over sulphuric acid, solidified to a yellow crystalline mass, which was purified by washing with a mixture of alcohol and ether, and crystallisation from alcohol.

Amido-isobutylformic acid crystallises in colourless plates, which are easily soluble in water, but difficultly soluble in alcohol and ether. When heated, it volatilises without melting. In these properties, it agrees entirely with Clark and Fittig's amido-valeric acid (*Annalen*, **139**, 200).

Oxyisobutylformic acid, $C_4H_8(OH).COOH$, is obtained by boiling bromisobutylformic acid with a slight excess of concentrated potash for a short time. After separating the potassium bromide and acidifying with strong hydrochloric acid, a yellow oil separates, which consists essentially of isobutylformic acid; this is removed, and the oxyisobutylformic acid extracted from the acid liquid by agitation with ether; on distilling off the latter, a yellow syrup remains, from which colourless crystals separate after some time. The acid may be purified by crystallisation from ether. Oxyisobutylformic acid (m. p. 82°) and its salts do not differ in any of their properties from those of the oxy-acid and salts obtained by Clark and Fittig (*loc. cit.*) from ordinary valeric acid.

Ethyl oxyisobutylformate, $C_5H_9O_3.C_2H_5$, is obtained by the action of ethyl iodide on the silver salt. It is a colourless liquid of pleasant odour, and is lighter than water, in which it is but little soluble. It boils at 175° with slight decomposition. Treated with phosphorus trichloride, it does not give, as was expected, an acid identical or isomeric with angelic acid, but amorphous phosphides and a highly chlorinated oil.

Valerolactide, $C_5H_8O_2$, is obtained when oxyisobutylformic acid is heated in sealed tubes at 200° for 6 hours, thus :—$C_5H_{11}O_3 = C_5H_8O_2 + H_2O$. It crystallises in white needles (m. p. 136°; b. p. 220—240°), which are insoluble in cold water, and in hot water melt to a colourless oil. It is easily soluble in alcohol and ether; and may be sublimed in silky needles. It is not attacked by dilute alkaline solutions. T. C.

Isoheptylic Acid from β-Hexyl Iodide. By O. Hecht and J. Munier (*Deut. Chem. Ges. Ber.*, **11**, 1781—1782).—The nitril formed by the action of potassium cyanide on hexyl iodide from mannite yields an isoheptylic acid (b. p. 211—213°), which is oxidised by a mixture of potassium dichromate and sulphuric acid, to carbonic, acetic, and butyric acids.

Hence the authors consider that isoheptylic acid has the constitution $CH_3.CH(COOH).(CH_2)_3.CH_3$, and that β-hexyl iodide may be represented by the formula $CH_3.CHI.(CH_2)_3.CH_3$. W. C. W.

Dehydromucic Acid. By R. Heinzelmann (*Liebig's Annalen*, **193**, 184—194).—This acid is best obtained by heating mucic acid with an excess of hydrobromic acid in sealed tubes for about two days; it may be purified by means of the barium salt. The following equation represents its formation from mucic acid: $C_6H_{10}O_8 = C_6H_4O_5 + 3H_2O$. The acid is difficultly soluble in cold but more easily in boiling water, from which it crystallises in long silky colourless needles. It is less soluble in alcohol than in water, and almost insoluble in ether. On careful heating it sublimes without melting, but decomposes when quickly heated.

The *barium salt*, $C_6H_2O_5Ba + 2\frac{1}{2}H_2O$, is moderately soluble in hot water, but difficultly soluble in cold. It crystallises in needles; it loses 2 mols. of water at 130°, and the remainder at 180°.

The *calcium salt*, $C_6H_2O_5Ca + 3H_2O$, resembles the barium salt.

The *silver salt*, $C_6H_2O_5Ag_2$, is a white precipitate, which is but little soluble in cold water, and blackens in boiling water.

Ethyl dehydromucate, $C_6H_2O_5(C_2H_5)_2$, crystallises in colourless rhombic prisms (m. p. 47°), which are difficultly soluble in cold alcohol, but easily in hot. The alcoholic solution has a tendency to form supersaturated solutions.

An attempt to prepare an acetyl-compound by the action of acetic anhydride on the ethyl salt was unsuccessful; showing that dehydromucic acid does not contain an alcoholic hydroxyl-group, and therefore that it is not a triatomic acid.

Dehydromucic acid when exposed to a high temperature under pressure splits up into carbonic anhydride and pyromucic acid, thus: $C_6H_4O_5 = C_5H_4O_3 + CO_2$.

This shows that dehydromucic acid stands to pyromucic acid in the same relation as malonic acid to acetic acid, and succinic acid to propionic acid, &c.

Dehydromucic acid easily unites with hydrogen to form two isomeric crystalline acids of the composition $C_6H_6O_5$, the examination of which is not yet complete. T. C.

Trimethylcarbamine. By W. Rudneff (*Deut. Chem. Ges. Ber.*, **11**, 1938—1939.)—It is only monobasic acids which yield stable salts with this carbamine; normal salts of bibasic acids are decomposed on evaporating their aqueous solution, thus the normal sulphate is partly resolved into the hydrogen sulphate.

It unites at ordinary temperatures with tertiary butyl iodide to form the compound $(C_4H_9)_2HN.HI$, which on distillation with potash solution yields *mono-* not *di-*butylamine, thus: $(C_4H_9)_2HN.HI + KOH = C_4H_9.NH_2 + KI + C_4H_8 + H_2O$. The author is engaged in further investigation of this and of dimethylethylcarbamine; the latter being obtained as a bye-product in the preparation of dimethylethyl-acetic acid. C. F. C.

Acetylene Carbamides. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 1784—1787).—In a previous paper (*Ber.*, **10**, 1923) the author described the formation of a white and a yellow compound, both having the composition $C_4H_6N_4O_2$, which were obtained by the action of glyoxal on carbamide, in presence of hydrocyanic acid. He now finds that the two bodies are not isomeric, but that the difference in their properties was caused by the presence of a small quantity of an unknown substance in the yellow acetylene carbamide.

W. C. W.

Uric Acid Formula. By R. Fittig (*Deut. Chem. Ges. Ber.*, **11**, 1792—1793).—A purely personal discussion between the author and Willgerodt. W. C. W.

Paradipropylbenzene and its Derivatives. By H. Körner (*Deut. Chem. Ges. Ber.*, **11**, 1863—1867).—The author obtained this hydrocarbon by the action of sodium on a mixture of paradibromobenzene and propyl bromide. It is a colourless, highly refracting, aromatic liquid, boiling at 220—222°.

Paradipropylbenzene-sulphonic acid, $C_6H_3(C_3H_7)_2.HSO_3$, crystallises in colourless hygroscopic needles which melt at 62.° The lead salt crystallises with 1 mol. H_2O in radiating tufts of silvery needles; the barium salt with $\frac{1}{2}$ mol. of H_2O in slender needles; the calcium salt with 9 mols. H_2O in large colourless rhombic prisms.

Dinitroparadipropylbenzene, $C_6H_2(C_3H_7)_2(NO_2)_2$ (m. p. 65°), is obtained by introducing the hydrocarbon slowly into cold concentrated nitric acid. It crystallises in large colourless plates. With a mixture of sulphuric and nitric acids, a nitro-derivative is obtained which crystallises in needles.

Propylbenzoic acid, $C_6H_4(C_3H_7)COOH$ (m.p. 54°), is formed by the oxidation of the hydrocarbon with dilute nitric acid (1 in 4 by vol.). It crystallises from the hot aqueous solution in small monoclinic prisms, which melt at 140°, and sublime in the form of long needles. The barium salt crystallises with 2 mols. H_2O in large white plates; the calcium salt with 3 mols. H_2O in slender white needles.

C. F. C.

Bromination of Aromatic Hydrocarbons in Presence of Aluminium Bromide. By G. Gustavson (*Bull. Soc. Chim.* [2], **30**, 435).—By treating a solution of aluminium bromide in benzene or toluene with hydrobromic or hydrochloric acid gas, or with sulphuric acid, liquids are obtained, having the formulæ $Al_2Br_6.6C_6H_6$ and $Al_2Br_6.6C_7H_8$. The sp. gr. of the former at 0° is 1·49, and that of the latter at 0° 1·37. Bromine acts very energetically on these bodies, and in the case of the toluene compound, pentabromotoluene, $C_6Br_5.CH_3$, was obtained. The author considers that the part played by the hydrobromic acid in the formation of these bodies is similar to that played by mineral acids in the etherification of the alcohols and organic acids. The absorption of the hydrobromic acid is accompanied by a disengagement of heat, which is the cause of the formation of the new bodies with absorption of energy. Thus the substitution of bromine for hydrogen in the aromatic hydrocarbons is preceded by the formation of compounds analogous to $Al_2Br.6C_6H_6$ and $Al_2Br_6.6C_7H_8$. The author considers

these bodies exist and take part in all the reactions taking place in the presence of aluminium bromide described by Friedel and Crafts, and that their existence should form the starting point of this explanation, and not $C_6H_5Al_2Br_6$, which has only a hypothetical existence. L. T. O'S.

Chloranilines. By F. Beilstein and A. Kurbatow (*Deut. Chem. Ges. Ber.*, **11**, 1860—1863).—1. The authors have completed the series of dichloranilines by the preparation of the three hitherto unknown isomerides.

Orthodichloranilines, [NH_2:Cl:Cl = 1 : 3 : 4] from the corresponding nitrodichlorobenzene (m. p. 43°), and also by chlorinating metachloraniline. By replacing the NH_2 by chlorine, ordinary unsymmetrical trichlorobenzene is obtained. The acetanilide melts at 120·5°.

[NH_2 : Cl : Cl = 1 : 2 : 3] from the corresponding nitrodichlorobenzene. By substituting chlorine for the NH_2 group [1 : 2 : 3] trichlorobenzene is formed.

Metadichloraniline [NH_2: Cl: Cl = 1 : 2 : 6] also from the corresponding nitrodichlorobenzene (m. p. 71°).

The physical constants of the several isomerides and their acetyl derivatives are tabulated below.

	NH_2.	Cl.	Cl.	Melting-point.	Boiling-point.	Acetyl derivative. Melting-point.
Para..	1	2	5	50°	251°	132°
Ortho.	1	3	4	71·5°	272°	120·5°
	1	2	3	23·5°	252°	56·5
Meta .	1	2	4	63°	245°	143°
	1	3	5	50·5°	260°	186·5°
	1	2	6	39°	—	175°

By chlorinating para- or ortho-chloraniline, ordinary metachloraniline is obtained. Metachloraniline yields para- and (1 : 3 : 4) ortho-dichloraniline.

2. *Trichloranilines.*—The isomeride [NH_2 : Cl: C : Cl = 1 : 2 : 4 : 6] is prepared by chlorinating dichloraniline in acetic acid solution. It crystallises in long needles (m. p. 77·5°, b. p. 262°). The acetyl derivative melts at 204°.

[NH_2:Cl:Cl:Cl = 1 : 2 : 4 : 5] (m. p. 95—96°) is prepared by chlorinating paradichloracetanilide. By replacing the NH_2 group by chlorine, ordinary symmetrical tetrachlorobenzene is obtained. The acetyl derivative melts at 184—185°.

[NH_2 : Cl : Cl : Cl = 1 : 2 : 3 : 4] is formed, together with the preceding isomeride, by chlorinating metachloraniline in acetic acid solution. The relative insolubility of the acetyl derivative of the latter in dilute acetic acid (50 per cent.) afford an easy means of separation of the isomerides. It crystallises in needles, m. p. 67·5°, b. p. 292°. By substituting Cl for NH_2, [1 : 2 : 3 : 4] tetrachlorobenzene is formed. The acetyl derivative melts at 121°.

3. *Tetrachloranilines.*—The isomeride [NH_2 : Cl_4 = 1 : 2 : 3 : 4 : 6] is obtained by chlorinating metachloraniline. It crystallises in needles,

m. p. 88°. By treatment with ethyl nitrite, it yields the unsymmetrical tetrachlorobenzene (m. p. 50—51°). The acetyl derivative melts at 173—174°, and is not decomposed by warming with concentrated sulphuric acid.

[$NH_2 : Cl_4 = 1 : 2 : 3 : 4 : 5$] is prepared from the corresponding *nitrotetrachlorobenzene*. The crystals melt at 118°.

[$NH_2 : Cl_4 = 1 : 2 : 3 : 5 : 6$] (m. p. 90°) is also prepared from the corresponding nitrotetrachlorobenzene. C. F. C.

Formation of Chlorophenylene-diamine. By F. Beilstein and A. Kurbatoff (*Deut. Chem. Ges. Ber.*, **11**, 1939).—The product of the reducing action of stannous chloride on $C_6H_3Cl(NO_2)_2$ (m. p. 50°) the authors find to be chlorophenylene-diamine (m. p. 86°), and not $C_6H_3Cl(NO_2).NH_2$, as stated by Jungfleisch. C. F. C.

Malachite-green. (*Chem. Centr.*, 1878, 587.)—This aniline colour is said to possess many advantages over methyl-green. It is prepared by the action of dimethylaniline, $NC_6H_5(CH_3)_2$, on trichlorotoluene, $C_6H_5.CCl_3$, in presence of metallic chlorides. It is much cheaper than methyl-green, and is less affected by soap and by acids.

M. M. P. M.

Vanillo-diacetonamine. By W. Heintz (*Liebig's Annalen*, **194**, 53—67).—Acetaldehyde and benzaldehyde convert the hydrogen diacetonamine oxalate, on continuous boiling in alcoholic solution, into the normal oxalate aldehyde-compounds of diacetonamine, which dissolve with great difficulty in the boiling solution, and separate out. The attempt to extend this reaction further with other aldehydes was made. It was also hoped especially to get bases still richer in oxygen, by employing more highly oxidised bodies. This expectation was not realised as far as salicylic aldehyde is concerned, although indications were obtained that a basic substance is produced in small quantity: with vanillin, however, the action is the same as with dibenzaldehyde.

Equal parts of vanillin and acid diacetonamine oxalate were boiled with ten parts of alcohol for several hours with a reversed condenser. In this manner a fine white powder separates out, consisting of the normal oxalate of the new base, which is named vanillo-diacetonamine. The separated solution can be used for preparing fresh quantities of salt, but the unaltered vanillin must be removed by distilling off the alcohol and shaking up with ether. In the ether solution some vanillo-diacetonamine dissolves, doubtless in combination with ethyl-oxalic acid, whilst the aqueous solution separated by means of the tap-funnel contains the greatest amount of the base. From the ether solution it may be separated by continuously boiling the residue (after distilling off the ether) with water, and addition of some oxalic acid. By shaking with ether, the vanillin and an extraordinarily beautiful red substance are separated. The aqueous solution exactly neutralised with lime, filtered, and evaporated, deposits the vanillo-diacetonamine, together with a yellowish-red substance. The latter is mostly removable by boiling alcohol. The above-mentioned aqueous solution, still containing considerable quanti-

ties of the base, is diluted with water and boiled with oxalic acid for some time, and then filtered. The filtrate is evaporated, previously almost neutralised with lime, and filtered. The residue extracted with alcohol gives a red solution and a white crystalline substance—almost pure vanillo-diacetonamine oxalate. The latter is purified from admixed ammonium oxalate by boiling with a small quantity of water. The ammonium oxalate is much more soluble in boiling water than the vanillo-diacetonamine salt. By quickly drawing off the hot solution and repetition of this operation the salt remains quite pure.

Vanillo-diacetonamine Oxalate.—The salt whose preparation has been just described is the normal one, and it is not soluble either in alcohol or in ether; it is also only slightly soluble in water. If the salt be boiled with a quantity of water insufficient for solution, and for a long time, this solution becomes intensely yellow. The salt melts with partial decomposition and browning, and evolution of gas bubbles. Heated in tubes it yields a yellow tarry mass, and a small quantity of a substance in colourless needle-shaped crystals sublimes. The attempt to prepare an acid vanillo-diacetonamine oxalate was a failure.

Vanillo-diacetonamine appears to be a thick oily substance, obtained by decomposing the oxalate with milk of lime or excess of sodium carbonate solution. In the former case the solution becomes intensely yellow. It is filtered hot, and a stream of carbon dioxide passed through the solution, whereby the excess of lime is separated, and with it a small quantity of a dark-coloured, partially crystalline substance, not containing carbonic acid. Thus the base appears to be more soluble in lime water than in pure water. If sodium carbonate be used, a greenish-yellow precipitate separates, and the solution remains intensely yellow. The mixture was evaporated on the water-bath, when a brown mass remained. By evaporation in a vacuum a yellow residue is obtained, from which the free base may be extracted by alcohol. On evaporating this in a vacuum an amorphous residue remains, of a yellow or greenish tint, and of the consistence of turpentine. The body is soluble in alcohol and ether, but most so in the former. From analyses of the salts the author draws the conclusion that the formula of this base is $C_{14}H_{19}NO_3$. The base manifests an alkaline reaction, and was proved free from carbonic acid; also, by neutralising with oxalic acid, the characteristic neutral oxalate was again obtained.

Vanillo-diacetonamine Sulphate.—Prepared by boiling the oxalate with pure calcium sulphate. It crystallises from its hot aqueous solution in microscopic rectangular plates, insoluble in strong, but soluble in dilute alcohol; insoluble in ether. On heating in a tube, the salt first gives off a trace of water, then melts, with slight carbonisation and evolution of gas bubbles. A crystalline sublimate is also formed, with a small quantity of a tarry or oily body of empyreumatic odour. The salt is easily soluble in boiling water, and the hot concentrated solution deposits a portion on cooling.

Vanillo-diacetonamine Hydrochloride.—Prepared by decomposing the oxalate with calcium chloride. It crystallises in fine microscopic needles, which are easily soluble in alcohol, but separate on adding ether, in small spherical grains. It is purified from traces of calcium

chloride, by repeated precipitation from the alcoholic solution by means of ether.

This salt may also be prepared by dissolving the free base in dilute alcohol, and only just acidifying the solution with hydrochloric acid, and then evaporating in a vacuum. Excess of acid and heat must be avoided in thus preparing this salt or decomposition ensues.

Vanillo-diacetonamine Platinochloride.—Obtained as a brownish-red sticky precipitate by treating the hydrochloride with a slight excess of platinic chloride. The solution evaporated in a vacuum yields a sticky uncrystalline residue soluble in alcohol. The clear solution can be precipitated by ether. By a repetition of this process the body is obtained pure. The formula, reckoned from the platinum contained in the salt, is given as $(C_{14}H_{19}NO_3.HCl)_2.PtCl_4$.

Vanillo-diacetonamine Nitrate.—Prepared by distributing the extremely finely powdered oxalate through water, and adding the mixture to the equivalent quantity of lead nitrate, 1·77 parts of the oxalate to 1 part of the lead nitrate. By agitation and gentle warming a heavy thick precipitate is formed, sinking quickly to the bottom of the vessel. The latter is lead oxalate. The solution remains of a yellow colour. If the filtered yellow solution be evaporated in a vacuum, small crystalline masses are formed, consisting of small prisms and rectangular plates. They were purified by solution in boiling alcohol and precipitation with ether. To the cold alcoholic solution a considerable amount of ether may be added without turbidity arising, but on standing, such a solution deposited almost colourless crystals. This nitrate melts on heating, with decomposition. It is not very soluble in water, and this solution deposits small prismatic yellow-coloured crystals. These are moderately soluble in alcohol, and the solution is colourless. The salt is insoluble in ether. When crystallised from water it takes up 1 mol., which is again given up easily at 100°. The formula of this salt is then more fully $C_{14}H_{19}NO_3HNO_3.H_2O$.

Analyses show that vanillo-acetonamine has the empirical formula $C_{14}H_{19}NO_3$, and that it furnishes a mon-acid basic radicle. Its formation may be thus represented:—

$$\underset{\text{Diacetonamine.}}{C_6H_{13}NO} + \underset{\text{Vanillin.}}{C_8H_8O_3} = H_2O + C_{14}H_{19}NO_3.$$

and is quite analogous to that of the acetaldehydo- and benzaldehydo-diacetonamines. The structure of these three bodies, however, is as much enveloped in mystery as that of the triacetonamine. It is only probable that all four bodies are constituted alike. W. S.

Amidines and Thiamides of Monobasic Organic Acids. By A. Bernthsen and H. Trompetter (*Deut. Chem. Ges. Ber.*, **11**, 1756—1761).—The following amidines were prepared by the process already described (*Ber.*, **9**, 429; **10**, 1235; and this Journal, 1876, **2**, 95, and 1878, 70).

Ethenyltolylamidine, $CH_3.C(NH).NH.C_7H_7$, crystallises from a mixture of petroleum spirit and common ether in thin white prismatic

tables, which melt at 95·5—96°, and are easily soluble in alcohol, ether, and benzene. The oxalate, $C_9H_{12}N_2.C_2O_4H_2$, and the platinum salt, $(C_9H_{12}N_2HCl)_2PtCl_4$, are soluble in water and in hot alcohol.

Benzenylnaphthylamidine, $C_6H_5.C(NH).NH.C_{10}H_7$, is deposited from an alcoholic solution in glistening plates, which melt at 141°, and sublime without decomposition. The oxalate and chromate are sparingly soluble in water.

Ethylnaphthylamidine, $CH_3.C(NH).NH.C_{10}H_7$, is a syrupy liquid, which solidifies at −15°, but has not been obtained in the crystalline state. It is soluble in the ordinary solvents, and forms crystalline salts with hydrochloric, sulphuric, and oxalic acids. The nitrate is an oily liquid.

Diamines are also capable of uniting with organic cyanides, *e.g.*, *benzenyltolylamidotolylamidine*, $C_6H_5.C(NH).NH.C_6H_3(CH_3).NH_2$, or $C_{14}H_{15}N_3$, is formed by heating benzonitrile with α-toluylenediamine dihydrochloride at 180°. This body crystallises in small white needles (m. p. 212°), soluble in alcohol and in ether. Its salts are crystalline. The chromate is insoluble.

Benzenyltolyleneamidine, $[C_6H_5.C(NH).NH]_2C_6H_3.CH_3$, obtained by heating equivalent quantities of benzonitril and α-tolylenediamine monohydrochloride, is an oily liquid which slowly solidifies to an amorphous mass, which is very soluble in alcohol. The hydrochloride has not yet been obtained in the crystalline state. Its solution stains the skin yellow.

Amidines are converted into thiamines by the action of carbon bisulphide at 100°, according to the following equation :—

$$2RC(NH)NHR' + CS_2 = RC(S)NHR' + RC(NH)NHR.CNSH.$$

The following thiamides were prepared:—

Acetothiotoluidide, $CH_3.CS.NH.C_7H_7$, prepared by the action of carbon bisulphide on ethenyltolylamidine, or by the action of sulphuretted hydrogen on ethenylditolylamidine, crystallises from dilute alcohol in small yellowish-white prisms (m. p. 128°). *Benzonaphthylthiamine*, $C_6H_5.CS.NH.C_{10}H_7$, bright yellow plates (m. p. 147·5°). *Acetonaphthylthiamide*, $CH_3CS.NH.C_{10}H_7$, tabular yellowish crystals, m. p. 96°. *Benzamidotolylthiamide*, $C_6H_5.CS.NH.C_6H_3(CH_3).NH_2$, melts at 197°.

Reducing agents easily desulphurise substituted thiamides, *e.g.*, *benzylphenylamine* is obtained from benzothianilide, and *ethylnaphthylamine* from acetonaphthylthiamide. In the same way *benzyldiphenylamine* may be prepared from benzodiphenylthiamide. It crystallises in long white needles (m. p. 87°), which are sparingly soluble in water and in cold alcohol, but dissolve readily in ether and in hot alcohol.

W. C. W.

Imidothio-ethers. By A. Pinner and F. Klein (*Deut. Chem. Ges. Ber.*, **11**, 1825). — The hydrochloride of an imidothio-ether, RC(NH)SR, is formed when hydrochloric acid is passed into a mixture of a nitrile and a mercaptan, *e.g.*, *benzimido-thiamyl ether*, $C_6H_5.C(NH)S.C_5H_{11}$, is obtained in the form of a colourless mobile liquid by adding caustic soda to the product of the action of hydrochloric acid on benzonitril and amylmercaptan. W. C. W.

Action of Nitric Acid on Phenol and on Nitrophenols. By M. Goldstein (*Deut. Chem. Ges. Ber.*, **11**, 1943—1944).—The following points in connection with these actions are noticed :—

(1.) The ratio of the quantity of the more to that of the less volatile of the isomeric nitrophenols, obtained by the action of nitric acid on phenol, bears, within certain limits, a direct proportion to the temperature employed.

(2.) The author denies Fritsche's observation (*Bull. Acad. Sc. St. Pet.*, **3**, 215) of the formation of hydrocyanic acid and ammonia by the action of nitric acid on aqueous phenol.

(3.) By the action of concentrated nitric acid on orthonitrophenol, the author has obtained a crystalline body (m. p. 105°) which dissolves in hot water to an intensely yellow solution, having a bitter taste; it is under further investigation.

(4.) A rapid method for preparing dibromonitrophenol from orthonitrophenol consists in adding aqueous bromine to its alkaline solution until no further separation of the product is observed. On filtering, the almost perfectly pure dibromonitrophenol (m. p. 117°) is obtained.

C. F. C.

Dibenzoyl-dinitro-phenol. By M. Goldstein (*Bull. Soc. Chim.* [2], **30**, 434).—Dinitrodiphenol obtained by oxidising nitrophenol (m.p. 45°), $2C_6H_4(NO_2)(OH) - H_2 = C_{12}H_6(NO_2)_2(OH)_2$ yields a dibenzoyl-compound, $C_{12}H_6(NO_2)_2(C_7H_5O_2)_2$, which crystallises in needles, melting at 191°. The author has not succeeded in obtaining dinitrodiphenols from the isomeric phenols.

L. T. O'S.

Phenoldidiazobenzene. By Caro and Schraube (*Chem. Centr.*, 1878, 558).— This compound was regarded by Griess as $C_6H_3.(C_6H_5.N{=}N)_2OH$; by the action of the diazo-compound of diamidobenzene on potassium phenylate the authors have obtained $C_6H_4(OH.C_6H_4.N{=}N)C_6H_5.N{=}N$, a body isomeric with that prepared by Griess. The new compound yields aniline, paradiamidobenzene, and paramidophenol by the action of nascent hydrogen. The diazo-compound of diamidobenzene reacts generally in a manner analogous to that of diazobenzene itself.

M. M. P. M.

Hydrogen-phenyl Sulphate and similar Derivatives of the Phenols. By E. Baumann (*Deut. Chem. Ges. Ber.*, **11**, 1907—1916).— The author prepares phenyl-potassium sulphate by the following reaction: $K_2S_2O_7 + C_6H_5.OK = K_2SO_4 + SO_2OK.(OC_6H_5)$, observing special precautions for preventing the conversion of the potassium pyrosulphate into hydrogen potassium sulphate, and the occurrence of the reaction, $KHSO_4 + C_6H_5.OK = K_2SO_4 + C_6H_3.OH$. The sulphate crystallises from alcohol in small shining plates, from dilute alcohol in large transparent rhombic plates, which are soluble in seven parts of water at 15°. Exposed to moist air it is decomposed: $C_6H_5.O.OK.SO_2 + H_2O = C_6H_5.OH + KHSO_4$. Its solution is similarly decomposed by strong mineral acids at a gentle heat, and by acetic acid on long boiling; decomposition by the latter is prevented by the presence of alkaline salts, and this fact is of importance in the quantitative

estimation of ether sulphuric acids in urine. It is not decomposed in putrefying solutions. It is attacked with difficulty by strong alkalis, even at high temperatures. Heated to 150—160° it is largely converted by molecular rearrangement into the paraphenylsulphonate, $C_6H_5O.OKSO_2 = OH.C_6H_4.SO_3K$. The latter salt when pure forms anhydrous six-sided plates, the corresponding barium salt with three mols. H_2O, crystallises in needles. The above transformation suggests, by analogy, the following simple explanation of the formation of oxybenzoic acids by Kolbe's reaction:—

$$C_6H_5ONa + CO_2 = C_6H_5O.CO.ONa$$
$$C_6H_5O.CO.ONa = OH.C_6H_4.CO.ONa,$$

a view which as simply explains the fact of the conversion of only one-half the phenol into oxybenzoic acid by showing the probability of the following secondary reaction:—

$$OH.C_6H_4.CO.ONa + NaOH = C_6H_4.ONa.CO.ONa + H_2O$$
$$C_6H_5.O.CO.ONa + H_2O = C_6H_5.OH + HNaCO_3.$$

Attempts to prepare the potassium phenylcarbonate proved unsuccessful, however.

Sodium phenylsulphate is very unstable in solution; it is obtained in the form of needles by precipitating its aqueous solution with ether.

Cresolsulphuric Acid, $CH_3.C_6H_4O.SO_2OH$.—The potassium salt of this para-acid may be obtained in quantity from horses' urine, and is probably a constituent of the urine of other mammals. It is similar in its appearance and reaction to the phenylsulphate. The salt of the ortho-acid is obtained by the action of potassium pyrosulphate on the corresponding cresol.

Both are converted into sulphonates at 140—150°; solutions of the latter give a deep blue colour with ferric chloride.

Ether-sulphuric Acids of Dioxybenzene, $C_6H_4(O.SO_2.OH)_2$ and $C_6H_4(OH)O.SO_2.(OH)$.—The method of preparation of the potassium salt of the first of these acids from resorcin is essentially similar to that employed in the case of the mohydic phenols. It crystallises in slender anhydrous needles, which are freely soluble in water.

The aqueous solution gives no reaction with ferric chloride, and may be evaporated with acetic acid without decomposition; but hydrochloric acid decomposes it completely into resorcin and sulphuric acid. The barium salt, $C_6H_4(SO_4)_2Ba$, is precipitated from its aqueous solution, in needles, on adding alcohol; its aqueous solution is decomposed on evaporation. The potassium salt is converted at 160° into a sulphonate. The acid was identified in the urine of dogs after they had swallowed 2—3 grams of resorcin.

The monoether sulphate is obtained from the mother-liquors from the preparation of the previous compound. It crystallises in thin colourless plates. The aqueous solution is decomposed on standing; it gives a violet colour with ferric chloride. Corresponding salts were obtained from pyrocatechin and hydroquinone.

Ether-sulphuric Acid of Trioxybenzene, $C_6H_3(OH)_2.O.SO_2OH$.—The potassium salt of the acid, prepared by the action of potassium pyrosulphate on pyrogallol, is easily soluble in water, but with difficulty

in alcohol. With ferric chloride the aqueous solution gives a deep green colour, which is changed to blue and violet on adding an alkali. This reaction is not distinguishable from that of pyrocatechin, and of those of its derivatives which retain the two OH. mols. intact; it is probable therefore that in the above compound they occupy the ortho-position.

Ether-sulphuric Acids of Oxybenzoic Acid, $C_6H_4(O.SO_2OH).COOH$.—The general method for the preparation of the potassium salts is here also applicable.

Ortho-compound.—This is permanent in the air, easily soluble in water, slightly in alcohol, and gives no coloration with ferric chloride. It is decomposed in aqueous solution by hydrochloric and by acetic acid, even in the cold; also by urine of acid reaction, and by human urine at 40°. Heated to 180—190° it is decomposed according to the equation—

$$C_6H_4(O.SO_2.OK).COOK = C_6H_4{<}\overset{O}{CO}{>} + K_2SO_4.$$

Other anhydrides are also formed.

Meta-compound.—This is found in the urine after swallowing meta-oxybenzoic acid. When heated it undergoes decomposition in a manner similar to the ortho-salt, but at 220—225° it is decomposed in aqueous solution by acids, although less easily than the ortho-salt.

Para-compound.—This salt crystallises in tables; its reactions are similar to those of its isomerides. It also occurs in urine under similar conditions.

Lastly, the author describes the corresponding derivative of gallic acid, $C_6H_2(OH)_2(SO_4K)COOH$. It crystallises in slender needles. Ferric chloride colours neutral solutions a bluish-green, closely resembling that obtained with protocatechuic acid. Hence it is probable that the two OH mols. occupy the ortho position.

C. F. C.

Action of Nitric Acid on Deoxybenzoïn. By Golubeff (*Deut. Chem. Ges. Ber.*, **11**, 1939).—By the action of fuming nitric acid (1·475) upon well-cooled deoxybenzoïn, two nitro-compounds are formed: $C_{14}H_{11}(NO_2)O$ (m.p. 141°), a crystalline body, insoluble in ether; and a second, which appears to be the dinitro-compound, $C_{14}H_{10}(NO_2)_2O$ (m.p. 120°). The former is reduced by tin and hydrochloric acid to an amido-deoxybenzoïn (m.p. 95—96°), apparently identical with that prepared from nitrobenzyl. The second also yields a crystalline base.

C. F. C.

Nitrobenzoic Acids. By F. Fittica (*J. pr. Chem.* [2], **13**, 184—228).—This paper is the concluding one of several in which the author contends that there are more than three series of bi-derivatives of benzene, and that, consequently, Kekule's benzene hypothesis does not possess the value assigned to it. Abstracts of previous papers will be found in this Journal, 1875, 766; 1876, **2**, 412; 1877, **2**, 483.

In the present paper the following points are specially maintained:—

(1.) That there exist benzene-derivatives which can be converted into each other by simple reactions after the manner of the usual

benzene-derivatives, but which do not fit in with any of the three known series: a nitro-benzoic acid, an amido-benzoic acid, and a nitro-benzaldehyde.

(2.) That nitro-benzoic acids exist, which have the same melting-point as the acid just mentioned, and the common metanitrobenzoic acid, but differ from them essentially in other physical properties.

The paper concludes with an account of a comparative investigation of the isomeric ethers of benzoic acid, and the molecular-compounds of nitrobenzoic acid with benzoic acid, and nitrobenzoic acid with amidobenzoic acid.

Mononitrobenzoic acid, melting point 127° (fourth nitrobenzoic acid).—This is prepared by dropping a mixture of benzoic acid (1 mol.) dissolved in pure anhydrous ether with ethyl nitrate (1 mol.) into concentrated sulphuric acid. It consists of tufts of small slightly yellowish needles, which dissolve in 379·7 parts of water at 16°, and are also easily soluble in alcohol and ether. It has a bitter taste. The *barium salt* consists of yellowish needles. The *ethyl salt* is obtained by dissolving the nitro acid at *ordinary* temperatures in ammonia, precipitating as silver salt, and acting on the latter with ethyl iodide. It consists of small inodorous needles of a pale yellow colour, which melt at 37—38°, and are soluble in alcohol and ether, but not in water.

Mononitrobenzoic Acid, melting point 136° (physically?).—Isomeric fourth nitrobenzoic acid is obtained by adding one part of powdered benzoic acid to two parts of colourless nitric acid (sp. gr. 1·4), the temperature being limited to 60°. It consists of small white needles in stellate groups, which are soluble in 373 parts of water at 16°. The *barium salt* dissolves with difficulty in hot water. It contains four molecules of water.

Amidobenzoic Acid from the fourth Nitrobenzoic Acid.—Nitrobenzoic acid, melting point 127 or 135°, is exactly saturated with dilute ammonia at ordinary temperature; the liquid is then acted on by sulphuretted hydrogen at 80°. A solution of ammonia is then added by degrees, the stream of sulphuretted hydrogen being still continued, until a filtered specimen is no longer precipitated by sulphuric acid after cooling. The melting point of this amidobenzoic acid varies between 154 and 160°. It dissolves in 29·3 parts of water at 16·5°, and is easily soluble in alcohol and ether, and is almost tasteless. Its formula is $C_6H_4(NH_2).COOH$.

The *lead salt*, $(C_6H_4(NH_2)COO)_2.Pb$, consists of a heavy amorphous powder, soluble in 400 parts of water. It is anhydrous.

Sulphuric acid compound, $(C_6H_4(NH_2).COOH)_2H_2SO_4 + H_2O$, obtained by the action of concentrated sulphuric acid on the amido acid, or by decomposing the compound of the amido acid with the fourth nitrobenzoic acid by dilute sulphuric acid. It consists of short, thick, yellowish prisms, which melt at 235°, and crystallise with one molecule of water.

The tin double salt, $(C_4H_6(NH_2).COOH.HCl)_2SnCl_2$, can be obtained either from the nitrobenzoic acid of melting point 127 or 135°, by warming it with tin and hydrochloric acid (limiting the temperature to 60°), or from the corresponding amido acid by means of stannous

chloride containing hydrochloric acid. It consists of small yellowish needles, easily soluble in water and in hot hydrochloric acid.

Nitrobenzaldehyde, corresponding with the fourth nitrobenzoic acid, is obtained by the action of concentrated sulphuric acid on a mixture of benzaldehyde and ethyl nitrate, with careful regulation of temperature. It consists of $C_6H_4(NO_2).COH$, forms a brownish-yellow oil, with a faint smell of benzaldehyde, and exhibits the ordinary properties of aldehydes. On oxidation with chromic acid it yields the fourth nitrobenzoic acid.

Lemon-yellow Nitrobenzoic Acid melting at 142°.—One molecule of benzoic acid is dissolved in six to eight times its weight of concentrated sulphuric acid, and a molecule of ethyl nitrate is added. The temperature must be 80—100°, and no decomposition of ethyl nitrate with evolution of red fumes must be allowed to take place. This acid, $C_6H_4(NO_2).COOH$, consists of small yellow needles, which melt at 141—142°, and dissolve in 309·1 parts of water at 16°. It has a bitter taste. The *barium salt* consists of acicular needles, with four molecules of water; the anhydrous salt is golden-yellow.

The *ethyl salt* is formed in the usual way, and consists of fine, large, yellow prisms, which melt at 41°. The *amido-compound* melts at 178°.

The *lead salt* of the last acid is anhydrous, and crystallises in lemon-yellow plates, which dissolve with difficulty. The *sulphuric acid compound* crystallises in silky white needles, and melts at 240°.

Lemon-yellow Nitrobenzoic acid melting at 128°, is obtained by acting on a mixture of benzoic chloride (1 mol.) and ethyl nitrate (1 mol.) with sulphuric acid. The temperature should be limited to 70—80°. It crystallises in lemon-yellow needles, which melt at 128°, and dissolve in 284·5 parts of water at 16°. It has a bitter taste. The *barium salt* consists of small bright yellow needles, which contain four molecules of water. It is electric when rubbed. The anhydrous salt is still more electric, and of an intense yellow colour.

The *ethyl salt* is prepared in the same way as its isomeride is from the nitrobenzoic acid, melting at 127°. It consists of small lemon-yellow prisms, melting at 38—39°, and is easily soluble in alcohol and ether.

The *amido-compound* is prepared in the same way as that from nitrobenzoic acid, m.p. 127°. It is of a brownish colour, and melts at 170°.

Lemon-yellow Nitrobenzoic Acid melting at 135°.—This modification is obtained by the action of ethyl nitrate on benzoic acid, dissolved in sulphuric acid at a temperature of 50—60°. It is chemically identical with the last-described acid, yielding the same ether and the same amido derivative, but differs from it in melting point and solubility, one part of it requiring for solution 340·9 parts of water at 16°.

Azobenzoic Acids.—Fittica has also prepared the ethyl salts of the azo-derivatives of the three known nitrobenzoic acids, in order to establish their isomerism. *Ethyl ortho-azobenzoate* forms deep red needles, melting at 138—139°; *ethyl para-azobenzoate* crystallises in reddish-yellow thick prisms, melting at 88°; and *ethyl meta-azobenzoate* forms reddish-yellow needles, melting at 99°.

The ethyl salt of the azobenzoic acid derived from the lemon-yellow nitrobenzoic acid which melts at 142°, was found to melt at 102°, whence Fittica regards it as different from the ether of meta-azobenzoic acids.

Benzo-nitrobenzoic Acids, $C_7H_6O_2.C_7H_5(NO_2)O_2$.—An *ethyl benzo-nitrobenzoate* may be prepared by dissolving one molecule of benzoic acid in ether free from water and alcohol, adding to the solution one molecule of ethyl nitrate, and dropping the mixture into pure concentrated, but not fuming, sulphuric acid. When the temperature produced by the reaction has risen to 50°, it must be kept at that point by cooling until the last drop of the mixed liquid has been added, and the mixture afterwards warmed in a water-bath at 50°, until it no longer solidifies on cooling. It is then to be poured into water; the ethereal layer pipetted off; the ether removed; the remaining oily or semi-solid mass washed with sodium carbonate; and the residual oil dried and distilled. Benzoic ether (m.p. 211°) then passes over first, next follow distillates from 250—290°, which deposit ethyl nitrobenzoate (m.p. 41°); and by repeated fractional distillation an *ethyl benzonitro-benzoate* $C_7H_5O_2(C_2H_5).C_7H_4(NO_2)O_2(C_2H_5)$, is finally obtained, as a liquid boiling at 282—285°, having a faint, somewhat pungent odour, not at all like that of benzoic acid, and yielding by saponification a benzonitrobenzoic acid, which melts at 136—137°, and solidifies at 130°. This acid is not decomposed by a current of steam; it dissolves in 861·8 parts of water at 16°, and is resolved in hot aqueous solution into benzoic acid, and the fourth nitrobenzoic acid. The same melting and solidifying point are exhibited by a benzonitro-benzone, and prepared from the lemon-yellow nitrobenzoic acids.

Lastly, the fourth nitrobenzoic acid forms with its amido-acid a molecular compound, $C_6H_4(NO_2)(COOH).C_6H_4(NH_2)COOH$, which melts at 156—158°, or at 158—160°; dissolves in 57·8 parts water at 16°, yields a lead salt, which dissolves in 390 parts of hot water, and when dry becomes strongly electric by friction. The compound acid treated with sulphuric acid is resolved into its constituent acids.

The lemon-yellow nitrobenzoic acid melting at 128° likewise unites with the corresponding amidobenzoic acid, forming a compound which also melts at 158—160°, but is less soluble than the preceding, requiring for solution 96·2 parts of water at 16°.

The final conclusion deduced by Fittica from the facts above detailed is that there exist six chemically different nitrobenzoic acids. G. T. A.

Note by the Editor.—The facts recorded in this paper add nothing to the evidence adduced by the author in previous communications (this Journal, 1876, **2**, 412; 1877, **2**, 483) in support of the existence of nitrobenzoic acids distinct from the three well-known modifications. With regard to the melting points, it has long been pointed out by Widnmann and by Leo Liebermann (*Deut. Chem. Ges. Ber.*, **10**, 1038, 1159), that mixtures of organic acids (like certain metallic alloys) often melt at temperatures lower than the melting points of either of their constituent acids, and that this is especially the case with mixtures of the *o*-, *m*-, *p*-nitrobenzoic acids, mixtures of which in certain

proportions exhibit melting points very near to those of Fittica's new nitrobenzoic acids. With regard especially to the "fourth" nitrobenzoic acid (m.p. 127°), it is to be observed that the author regards its existence as definitely established by its formation from the liquid modification of nitrobenzaldehyde (p. 152). But the separate identity of this latter body is by no means well established. There is nothing in its mode of preparation to show that it is not a mixture of two or three isomeric modifications; and this view derives some support from the fact that it is partly decomposed by distillation, even under a pressure of 50 m.m.; and that the distillate, which is at first light-yellow, quickly turns brown, a change which is not exhibited by the aldehyde before distillation. In short, the only evidence in support of the existence of this liquid nitrobenzaldehyde as a distinct modification, is its conversion into the *fourth* nitrobenzoic acid; and yet the author relies upon this very reaction to demonstrate the separate existence of the acid itself. H. W.

Isomeric Nitro- and Amido-benzoic Acids, and Formation of Chloranil from the latter. By E. Widnmann (*Liebig's Annalen*, **193**, 202—240).—The author finds that by nitrating benzoic acid with sulphuric acid and nitre, three, and only three, nitro-acids are produced, viz., meta-, ortho-, and para-benzoic acids; he is, therefore, unable to confirm Fittica's (*Ber.*, **8**, 252, 710, 741) results as to the formation of a fourth, fifth, and sixth nitrobenzoic acid. The three nitrobenzoic acids cannot be separated from one another as such, but only by means of the barium salts.

Meta-nitrobenzoic acid exhibits two different melting points, for it first melts at 140°, and resolidifies at about 117°; on reheating *directly* after *slow* cooling it melts at 135°, but after *quickly* cooling, or after *standing some hours* subsequent to slow cooling, it melts at 141°. This phenomenon explains Fittica's observation as to the existence of a nitrobenzoic acid melting at 135°, and possessing properties similar to those of the meta-acid. This double melting point is not affected even by heating the acid to 205°. The effect of the presence of water on the melting point was also investigated. On oxidation with sulphuric acid and potassium dichromate, meta-nitrobenzoic acid yields acetic acid and a volatile compound, which is soluble in ether, but has not been further examined.

Ortho-nitrobenzoic acid is less soluble in water than its barium salt, and crystallises in large colourless needles. It has an intensely sweet taste, sublimes slowly on heating, and is slightly volatile in steam. It does not melt under hot water. It possesses but one melting point, viz., 147° (Griess, 145°; Kulberg, 141°). The barium salt crystallises with three molecules of water. On oxidation with sulphuric acid and potassium dichromate it yields acetic acid.

Paranitrobenzoic acid melts at 238° (other observers 232—240°), but does not exhibit a double melting point. It has a bitter taste; on oxidation it gives acetic acid. The barium salt crystallises with five molecules of water.

The melting points of various mixtures of the different nitrobenzoic acids are given; a mixture of two of them in different proportions

shows a definite melting point, which is always below that of either of the constituents.

The three nitrobenzoic acids were converted into the corresponding amidoacids, the properties of which agreed in most respects with those observed by other investigators. The author found the melting point of the meta-amidobenzoic acid to be 174°; that of the ortho-compound 145°, and the para-amidoacid (amidodracylic acid) 186—187°.

All the three amido-benzoic acids yield a mixture of tri- and tetra-chlorquinone (chloranil) when treated with potassium chlorate and hydrochloric acid.

Stenhouse's observation that tetrachlorquinone is partly changed into trichlorquinone by the action of sulphurous acid is confirmed; from this it follows that tri- and tetrachlorquinone cannot be separated from one another by Graebe's method. T. C.

Sulphoparachlorobenzoic Acid. By T. Cöllen (*Liebig's Annalen*, **191**, 29—32).—This acid was prepared from parachlorobenzoic acid by Böttinger's method (**191**, 13—14); it crystallises from its aqueous solution in long needles, which are only slightly soluble in alcohol and ether. On heating it is decomposed with evolution of a small quantity of parachlorobenzoic acid. It forms acid and normal salts with the alkali metals. The normal potassium salt is very soluble in water, the acid salt crystallises in long needles; the acid sodium salt is very soluble in water, the solution having an acid reaction; it crystallises from its alcoholic solution in needles. The mercury salt crystallises in shining plates; is easily soluble in hot water, but with difficulty in cold. The barium salt crystallises in large plates; it is slightly soluble in water. Mg, Cn, Pb, and Zn salts are also described.

The monochloride of the acid, $C_6H_3Cl(SO_2Cl).COOH$, crystallises from ether in long needles, which melt at a temperature varying between 140—150°. C. F. C.

Substitution-products of Mesitylenic Acid. By H. J. Schmitz (*Liebig's Annalen*, **193**, 160—184).—By the action of nitric acid on mesitylenic acid, two nitro-derivatives are obtained, one of which gives a difficultly soluble barium salt, crystallising in tables; the other an easily soluble barium salt crystallising in needles.

α-Nitro-mesitylenic acid, $C_6H_2(NO_2)(CH_3)_2.COOH$, is the acid obtained from the easily soluble barium salt, and is produced in larger quantity than the *β*-acid. It crystallises from water in slender needles (m. p. 210—212°), which are very difficultly soluble in cold water. From alcohol or ether it separates in large triclinic prisms.

α-Barium salt, $(C_9H_8NO_4)_2Ba + 4H_2O$, crystallises in tufts of slender needles, which are easily soluble in cold water, and soluble in hot water in almost all proportions.

α-Calcium salt is soluble in water in all proportions, and crystallises in long needles.

α-Magnesium salt is soluble in water in all proportions, and separates on evaporation in crystalline crusts.

Ethyl α-Nitro-mesitylenate, $C_9H_8(NO_2)O_2.C_2H_5$, crystallises in large tables (m. p. 65°), which are insoluble in water, but easily soluble in alcohol.

β-Nitro-mesitylenic acid, $C_6H_2(NO_2)(CH_3)_2.COOH$, is obtained from the difficultly soluble barium salt above referred to. It is insoluble in cold water, and only very difficultly soluble in hot; it is easily soluble in hot alcohol, and separates therefrom on cooling in very large compact monoclinic crystals. This acid exhibits very characteristic properties on melting. The acid precipitated from the barium salt melts at 175°, but when crystallised from alcohol, it melts at 214—220°, and on cooling solidifies only at 162°, after which it fuses at 168° on reheating. If a trace of alcohol be added to this fused acid, even when heated over 200°, it solidifies immediately, and begins to melt again only at 214°.

β-Barium salt, $(C_9H_8NO_4)_2Ba + 4H_2O$, crystallises in monoclinic tables, which are difficultly soluble in cold water, but more easily soluble in hot water.

β-Calcium salt, $(C_9H_8NO_4)_2Ba + 6H_2O$, is difficultly soluble in hot water, and crystallises in long prismatic needles belonging to the monoclinic system.

Ethyl β-Nitro-mesitylenate, $C_9H_8(NO_2)O_2.C_2H_5$, crystallises in long needles or thick prisms (m. p. 72°), which are insoluble in water, but easily soluble in alcohol.

α-Amido-mesitylenic acid, $C_6H_2(NH_2)(CH_3)_2.COOH$, crystallises in long colourless needles (m. p. 186°).

β-Amido-mesitylenic acid, $C_6H_2(NH_2)(CH_3)_2.COOH$ (m. p. 235°), melts at about 235°, and is identical with the nitromesitylenic acid of Fittig and Brückner.

By the action of bromine on mesitylenic acid, two brominated derivatives are obtained, which are separated by the different solubilities of their barium salts.

α-Bromo-mesitylenic acid, $C_6H_2Br(CH_3)_2.COOH$, is produced in the largest quantity, and is obtained from the more soluble barium salt. It crystallises in rhombic prisms, which melt at 146°, resolidify at 131°, and remelt at 138°, in which respect it resembles the β-nitro acid. It is very difficultly soluble in cold, but easily soluble in hot water, and crystallises therefrom in slender needles. It is easily soluble in alcohol, from which it crystallises in large colourless prisms.

α-Barium salt, $(C_9H_8BrO_2)_2 + 4H_2O$, forms large colourless monoclinic crystals, which are easily soluble in hot and cold water.

α-Calcium salt, $(C_9H_8BrO_2)_2 + 2H_2O$, crystallises in slender needles, which are easily soluble.

β-Bromo-mesitylenic acid forms compact monoclinic crystals (m. p. 214°), which are difficultly soluble in hot water. It is identical with the acid obtained by Fittig and Storer.

β-Barium salt, $(C_9H_8BrO_2)_2Ba$, crystallises in colourless needles, which are difficultly soluble in cold water, but more soluble in hot.

The two nitro-compounds were converted by means of the diazo-reaction into the bromides, and the correspondence of the two α-compounds and of the two β-compounds directly proved. In order to determine the constitution of the two series of derivatives, the amido-

acids were converted into the corresponding xylidines by distillation with lime.

α-Metaxylidine, $C_6H_3(CH_3)_2.NH_2$, is a colourless oil (b. p. 212° uncorr.), identical with the α-xylidine of Hofmann and of Wroblewski.

α-Metaxylidine hydrochloride, $C_8H_9.NH_2.HCl$, is difficultly soluble in cold water, but more easily in hot, and generally crystallises therefrom in large prisms, but sometimes in tables.

α-Metaxylidine nitrate, $C_8H_9(NH_2).HNO_3$, forms large rhombic tables.

Acetyl α-metaxylidine, $C_8H_9.NH(C_2H_3O)$, is obtained by the action of acetyl chloride on α-metaxylidine. It crystallises in masses of needles (m. p. 127°).

β-Metaxylidine is a colourless oil (b. p. 216°).

β-Metaxylidine hydrochloride, $C_8H_9(NH_2).HCl$, is easily soluble in water, and crystallises from the hot solution on cooling in large thin plates, and by slow evaporation in colourless highly refractive monoclinic crystals.

Acetyl β-metaxylidine melts lower than the α-compound, and is more easily soluble.

Wroblewski, by displacing the amido-group in α-xylidine by bromine, has obtained a bromo-xylene [$CH_3 : CH_3 : Br = 1 : 3 : 4$]; and as in mesitylic acid the three side-chains have the positions [1 : 3 : 5], it results that the NO_2, NH_2, or Br in the α-series of compounds lies between the COOH-group and one of the CH_3-groups, and in the β-series between the two CH_3-groups. T. C.

Synthesis of Metanitrocinnamic Acid. By R. Schiff (*Deut. Chem. Ges. Ber.*, **11**, 1782—1783).—Metanitrocinnamic acid is formed by heating equal molecules of nitrobenzaldehyde, acetic anhydride, and sodium acetate, for 8 hours. The crude product is washed with water, and dissolved in dilute ammonia. Sulphuric acid precipitates the pure acid from this solution as a white crystalline powder (m. p. 196—197°), which yields metanitrobenzoic acid (m. p. 140°) on oxidation. W. C. W.

Oxypropylbenzoic Acid. By R. Meyer and J. Rosicki (*Deut. Chem. Ges. Ber.*, **11**, 1790—1792).—The acid was prepared by the oxidation of cuminol with potassium permanganate in alkaline solution, the yield being almost theoretical. The following salts of oxypropylbenzoic acid were examined:—$(C_{10}H_{11}O_3)_2Ba + H_2O$; $4C_{10}H_{11}AgO_3 + H_2O$; $(C_{10}H_{11}O_3)_2Cu + 3H_2O$. On boiling with dilute hydrochloric acid, this acid is converted into propenyl-benzoic acid,

$$C_6H_4(COOH).(CH_2)_3.OH = H_2O + C_6H_4(COOH)C_3H_5.$$

Propenyl-benzoic acid, $C_{10}H_{10}O_2$, melts at 160—161°, is sparingly soluble in hot, and insoluble in cold water. Its salts are mostly insoluble. The methyl ether, which was obtained by saturating a solution of oxypropyl-benzoic acid in methyl alcohol with hydrochloric acid, melts at 53° and boils at 254°. W. C. W.

Dioxybenzoic Acid. By L. Barth (*Deut. Chem. Ges. Ber.*, **11**, 1569—1571).—The author has described (this Journal, 1878, 61) two

bodies, $C_{12}H_{10}O_3$ and $C_{24}H_{18}O_5$, which he obtained from resorcin by the action of HCl, HI, &c., at a high temperature, the former of which gives a green, and the latter a blue fluorescence with alkalis. He has now obtained the same bodies from diethyldioxybenzoic acid by distillation with caustic lime (and for the most part the one represented by the formula $C_{12}H_{10}O_3$).

From these results and from the formation of metadicyanobenzene and isophthalic, and also dioxybenzoic acid from disulphobenzoic acid, as well as that of resorcin from dioxybenzoic acid, the author considers that both OH-groups occupy the meta position in this acid.

A. J. C.

Thymoloxycuminic Acid. By L. Barth (*Deut. Chem. Ges. Ber.*, **11**, 1571—1578).—The author has further investigated this acid, which is formed, together with oxybenzoic acid, oxyterephthalic acid, and an acid which precipitates lead acetate (thymolic acid), by fusing thymol with potassium hydrate (this Journal, 1878, 574). The separation of these four acids is effected by means of their different degrees of solubility in hot and cold water, thymoloxycuminic acid being very difficultly soluble in cold water. Its formula, $C_{10}H_{12}O_3$ (m. p. 141—143°), and crystalline characters as previously given, are confirmed. It readily dissolves in ether, alcohol, chloroform, and benzene, and to some extent in hot water, but is almost insoluble in cold water. It is monobasic, and forms neutral salts, which have a slightly acid reaction. Its aqueous solution gives no characteristic coloration with ferric chloride.

Normal sodium salt, $C_{10}H_{11}NaO_3$ (dried at 110—115°), or $4(C_{10}H_{11}NaO_3) + 9H_2O$ for the crystalline salt, which is obtained as a foliated crystalline mass, sometimes in well-formed needles, by incompletely neutralising the acid with sodium carbonate, and removing excess of acid by agitating with ether. It dissolves readily in water.

The basic sodium salt, $C_{10}H_{10}Na_2O_3$ (dried at 110°), is obtained by neutralising the acid with sodium hydrate. It crystallises in fine needles, which are very hygroscopic. When dried over sulphuric acid, it contains $1\frac{1}{2}$ molecules water of crystallisation.

Barium salt, $(C_{10}H_{11}O_3)_2Ba$. Crystallises in small prisms, and dissolves readily in water.

Cadmium salt, $C_{10}H_{10}CdO_3 + H_2O$. Crystallises in small colourless needles or plates; it is very soluble in water, and tolerably so in ether.

Ethyl salt, $C_{10}H_{10}(C_2H_5)O_3$. Formed on acting with hydrochloric acid on the alcoholic solution of the acid. It is an oily mass, which finally solidifies. The crystals are long prisms, without water of crystallisation (m. p. 73—75°).

The bromine derivative, $C_{10}H_{10}Br_2O_3$, is a white crystalline anhydrous mass, and appears to be a dibrominated acid.

Thymol-oxycuminic acid is capable with some difficulty of further oxidation by fusion with potassium hydrate, forming oxyterephthalic acid and the so-called thymolic acid.

The constitution of this acid may be represented either as $C_3H_7.C_6H_3(COOH)(OH)(C_3H_7) = 1:3:4$, which ought to give orthopropylphenol, or as $C_6H_3(CH_3)(OH)(C_3H_5O_2) = 1:3:4$, from which methyl-

ethylphenol should be obtained. But the attempts to convert the acid into these phenols were unsuccessful. The authors consider, however, that the first formula is more likely to be correct, as the acid gives no coloration with ferric chloride, and as a part of the acid is converted by heat into the anhydride, $C_{20}H_{22}O_5$, by the abstraction of water, according to the equation $2C_{10}H_{12}O_3 = H_2O + C_{20}H_{22}O_5$.

Oxybenzoic acid was obtained from the mother-liquor from which oxyterephthalic acid and thymol-oxycuminic acid had been separated. It is probably produced either from thymol by a direct action, or from oxyterephthalic acid by the continued action of the potash, as has been proved by the author's experiment. The so-called *thymolic acid* contains at least two bodies, and the subject is still under investigation.

The author has not been able to obtain from thymol the oxytoluylic acid which Jacobsen has described. A. J. C.

Quinic Acid. By R. Fittig and W. F. Hillebrand (*Liebig's Annalen*, **193**, 194—201).—By the action of acetic anhydride on ethyl quinate, *ethyl tetra-acetyl-quinate*, $C_6H_7.(OC_2H_3O)_4.COOC_2H_5$, is obtained. This reaction proves that quinic acid contains four alcoholic hydroxyl groups, thus: $C_6H_7(OH_4)_4.COOH$. Ethyl tetra-acetyl-quinate is almost insoluble in cold, and only difficultly soluble in boiling water; it dissolves easily in hot alcohol and ether. It crystallises from boiling water in plates (m. p. 135°), and can be sublimed without decomposition. By slow evaporation of the ethereal solution, it can be obtained in large colourless rhombic crystals.

Quinic acid heated with hydrobromic acid in sealed tubes at 130°, yields benzoic and protocatechuic acids, thus:—

$$2C_6H_7(OH)_4.COOH = C_6H_5.COOH + C_6H_3(OH)_2.COOH + 6H_2O,$$

together with small quantities of parabromphenol and hydroquinone. The above facts show that quinic acid is nearly related to hexahydrobenzene and quercite, thus:—

C_6H_{12}	$C_6H_7(OH)_5$	$C_6H_7(OH)_4.COOH$
Hexhydrobenzene.	Quercite.	Quinic acid.

T. C.

Malabar Kino and Kinoïn. By C. Etti (*Deut. Chem. Ges. Ber.*, **11**, 1879—1883).—Green kino is boiled with twice its weight of dilute hydrochloric acid (1 : 5); the solution is poured from the deposit of kino red (kinoroth) and shaken with ether; this removes a crystalline body, *kinoïn*, which is purified by recrystallisation from water, and is then obtained in the form of small colourless prisms, easily soluble in hot, with difficulty in cold water, readily in alcohol. These solutions may be evaporated unchanged, but are decomposed on standing in contact with the air. Kinoïn is anhydrous, and has the empirical formula, $C_{14}H_{12}O_6$. Heated at 120—130° until the weight becomes constant, it yields the anhydride $C_{28}H_{22}O_{11}$ (from 2 mols.), which the author finds to be identical with kino red. This anhydride, heated to 160—170°, loses another mol. H_2O, and becomes $C_{28}H_{20}O_{10}$. Both anhydrides are precipitated by gelatin; kinoïn is not.

Constitution of Kinoïn.—When this substance was heated with hydrochloric acid at 120—130°, methyl chloride escaped on opening the tube, and the solution contained pyrocatechine and gallic acid: hence the author describes kinoïn as a pyrocatechine methyl-gallic ether, which is consistent with the formula given above, $C_{14}H_{12}O_6$. Kino red yielded the same products of decomposition; it gave, on dry distillation, small quantities of phenol and pyrocatechin.

Melting point of Gallic Acid.—The gallic acid obtained as above by the action of hydrochloric acid on kino, crystallised in long silky prisms, gave all the reactions of gallic acid, analysed as $C_7H_6O_5H_2O$, but melted at 232° instead of 200°, its received melting point. The author then examined several preparations of gallic acid, and found them to have varying melting points, 222—232—240°; in no case lower than 222°. Pyrogallic acid prepared from these melted uniformly at 131°, and not at 115° or 118°, as usually stated. Stenhouse has also observed the melting point of this body to be 131·5° (*Ann. Chem.*, **179**, 236). These points need clearing up. C. F. C.

Chemical Constituents of the Willow, and its Pathological Formations. Certain Reactions with Tannins and Allied Substances. By E. Johanson (*Arch. Pharm.* [3], **13**, 103—130).—Seeing that tannin, gallic acid, quercitrin, &c., are contained in oak-galls and similar formations, it was thought probable that similar pathological formations produced by insects on other trees would also contain the same substances. Laminæ of healthy leaves and twigs of different willows were examined and compared with the same quantity of the pathological formations occurring on them. The substances were pounded, extracted with distilled water, the extract concentrated and filtered; the filtrate shaken up with ether to remove the gallic acid, &c. The residue, after extraction with water, was then treated with alcohol and concentrated, then freed from resin, chlorophyll, &c., by ether, the residue being again dissolved in alcohol, and upon this liquid the reactions were in part performed (D). After the separation of the ether extract from the original aqueous solution, the tannin was separated by lead acetate, and the precipitate decomposed by sulphuretted hydrogen (A). The filtrate from the precipitated lead acetate was employed for the detection of sugar, after separation of the excess of lead acetate (B). The ethereal solution being evaporated yielded, after separation of tannin, a residue soluble in water (C). The reactions of litmus, ferric chloride, lead acetate, silver nitrate, &c., upon the above solutions prepared from healthy and unhealthy plants, are fully detailed.

Solution A of the laminæ of *Salix alba* shows a different amount of tannin present; possibly quercitrin in the case of the unhealthy specimens. B shows that in the formations tannin has been converted into sugar. C yielded some substance, at present not known in like formations; probably quercitrin. In D was found some substance resembling quercitrin.

Salix viridis, var. *fragilis alba.*—A gave the same results as in the case of *Salix alba.* Sugar appears to be absent in the healthy specimens. C shows the presence of a small quantity of tannin, as well as

of gallic acid; it appeared possible that catechin might likewise be present. D indicates the presence of a quercitrin-like substance in the growths.

Salix fragilis alba, var. *fragilior*.—A does not appear to differ from other solutions obtained in the same manner. B again proves the presence of sugar in the growths. In D is found a larger amount of quercitrin-like substances.

Tannin appeared to be present in larger quantities in the leaf-stems than in the green twigs of another willow whose name is not given; but on this willow were found large growths, and these contained a smaller proportion of tannin. Sugar was found in larger quantities in the growths than in the stems, whereas it was absent in the leaves, being in inverse proportion to the tannin. It is doubtful whether gallic acid is present in the pathological formations, but the reactions are definite for the presence of quercitrin; the fact that gallic acid is produced in these growths from tannin is, however, proved. When the rind of the young twigs of *Salix acutifolia* is treated with alcohol, a substance is obtained possessing many of the properties of quercitrin, and is therefore probably allied to it. The tannins in the green parts of the plants, according to their nature, affect iron solutions differently; that which colours iron green is apparently an oxidation-product of that which colours iron blue, and the author considers that the latter, under the influence of transpiration, breaks up into the former modification and sugar. He likewise considers that the reverse process (that of reduction with introduction of sugar) is not possible, and as each tannin has its own special properties, these must be specially studied before the tannins can be systematically grouped. Tannin may be formed in the roots, stems, or twigs, or in the cells, without being restricted to any of the axial organs. It is then carried to the leaves and used in the process of vegetation. On the other hand, the tannin in the bark is most plentiful in autumn, when the stream of sap sets away from the leaves; consequently, we are led to the supposition that leaves manufacture the tannin-forming substance, which is carried downwards by the autumn stream of sap, and converted by the cells into tannin. E. W. P.

Mono- and Diphenyl-compounds of Arsenic. By W. La Coste and A. Michaelis (*Deut. Chem. Ges. Ber.*, **11**, 1883—1887).—By heating together arsenious chloride and benzene, the authors obtained a mixture of diphenyl (m. p. 70—71°) and *monophenylarsenious chloride*. The latter body was not separable as such from the diphenyl, but was identified by conversion into *monophenylarsenic acid*, $C_6H_5.AsO(OH)_2$. The following additional observations on the properties of this acid were made:—It begins to soften at 158°, giving off water and passing into an infusible anhydride, and at a higher temperature it is carbonised. It is unaffected by boiling with chromic acid, and is not reduced by zinc in acid or alkaline solution. The metals of the alkalis and alkaline earths yield salts of the form $C_6H_5.AsO(OH)(OM')$; only the heavy metals give normal salts. These are mostly amorphous; the barium salt crystallises in short radiating needles, the copper salt in pearly plates.

Monophenyltriethyl-arsenium iodide, $C_6H_5.As(C_2H_5)_3I$, is prepared by the action of zinc-ethyl on the product of the original reaction, separation of the phenyldiethyl arsine, and union of this with ethyl iodide. It melts at 112—113°. The corresponding hydroxide is obtained in the usual way, as a syrup, and the chloride yields a characteristic platinochloride.

Diphenylarsenious chloride, $As(C_6H_5)_2Cl$, is best obtained by heating mercury diphenyl (1 part) with monophenyl-arsenious chloride (3 parts) for several hours at 270°. Other products of this reaction are $Hg(C_6H_5)Cl$, $HgCl_2$, and *triphenyl-arsine*, $As(C_6H_5)_3$; the quantity of the latter is greater when the temperature is only slowly raised to and above 254°, its boiling point. The pure chloride is a yellowish oily liquid, of sp. gr. 1·422 at 15° C., which distils unchanged at 333° in a stream of carbonic anhydride. It unites with chlorine, forming *diphenyl-arsenious trichloride*, $As(C_6H_5)_2Cl_3$, which crystallises from benzene in large colourless plates. With bromine it yields the chlorobromide $As(C_6H_5)_2ClBr_2$, a comparatively unstable body.

Diphenyl-arsenious oxide, $[As(C_6H_5)_2]_2O$, is formed by heating the above chloride with alcoholic potash. It is a crystalline body, soluble in ether, and melting at 91—92°. Heated with concentrated hydrobromic acid it yields *diphenyl-arsenious bromide*, $As(C_6H_5)_2Br$, a yellowish oily liquid, boiling at about 356° with slight decomposition. Exposed to the action of chlorine gas it is converted into *diphenyl-arsenious oxychloride*, $[As(C_6H_5)_2Cl_2]_2O$ (m. p. 117°), a white powder, which is decomposed by water into HCl and the monobasic *diphenyl-arsenious acid*, $(C_6H_5)_2AsO.OH$. The lead salt of this acid crystallises from its aqueous solution in small silky needles.

Diphenyl-ethylarsine, $(C_6H_5)_2As(C_2H_5)$, is obtained by the action of zinc-ethyl upon diphenyl-arsenious chloride. It is a colourless liquid, with a fruity smell, boiling at 305°. It reacts with chlorine gas, forming the solid dichloride $(C_6H_5)_2As(C_2H_5)Cl_2$, which crystallises from benzene in long colourless needles. It combines with 1 mol. of ethyl iodide at 100° to form *diphenyl-diethyl-arsenium iodide*, $As(C_6H_5)_2(C_2H_5)_2I$. The corresponding chloride yields a characteristic platino-chloride.

C. F. C.

Triphenylarsine and its Derivatives. By W. La Coste and A. Michaelis (*Deut. Chem. Ges. Ber.*, **11**, 1887—1888).—This body crystallises in large rhombic plates (m. p. 58—59°) from the high-boiling residues from the preparation of diphenylarsenious chloride. It is most easily obtained from $C_6H_5.AsO$, which decomposes at 180—200° into As_2O_3 and $As(C_6H_5)_3$, thus: $3C_6H_5.AsO = As_2O_3 + As(C_6H_5)_3$. It distils unchanged in an atmosphere of carbonic anhydride at a temperature above 360°. It is easily soluble in ether and benzene, with difficulty in cold alcohol. It does not react with ethyl iodide at 100°.

Triphenylarsine dichloride, $As(C_6H_5)_3Cl_2$, is obtained by the action of dry chlorine upon the arsine, as a white powder. It crystallises from its solution in benzene in colourless plates (m. p. 171°); at 280° it is resolved into monochlorobenzene and $(C_6H_5)_2AsCl$. By the action of boiling water or dilute ammonia the chlorine atoms are replaced by OH groups; the *triphenylarsine hydroxide* thus formed, $As(C_6H_5)_3(OH)_2$,

crystallises from its aqueous solution in plates, from concentrated solutions in needles, which melt at 108°. Heated to 105—110° it loses 1 mol. of H_2O, and is converted into triphenylarsine oxide, $As(C_6H_5)_3O$.

Triphenylarsine forms with mercuric chloride the compound $As(C_6H_5)_3.HgCl_2$, a crystalline body, soluble in alcohol, but almost insoluble in water. It is not decomposed by aqueous potash in the cold, but on boiling the mercury is reduced to the metallic state, and $As(C_6H_5)_3(OH)_2$ is formed. By the action of alcoholic potash in the cold it is resolved into mercuric oxide and triphenylarsine, which dissolves in the alcohol. C. F. C.

Monotolyl Compounds of Arsenic. By W. La Coste and A. Michaelis (*Deut. Chem. Ges. Ber.*, **11**, 1888—1890).—*(Ortho)-monotolylarsenious Chloride*, $AsCl_2.C_7H_7$, is obtained by the action of (ortho) mercury-ditolyl upon arsenious chloride. It is a colourless liquid of feeble odour, boiling at 264—265°, and may be distilled unchanged in an atmosphere of carbonic anhydride. It is converted by chlorine gas into the tetrachloride $AsCl_4.C_7H_7$, a yellow liquid, which is decomposed by water into hydrochloric and monotolylarsenic acids. The corresponding para-compound is similarly obtained from (para) mercury-ditolyl (m. p. 235°). It crystallises in colourless plates, which melt at 31°, and distils unchanged in an atmosphere of carbonic anhydride at 267°. The tetrachloride solidifies at a slightly reduced temperature: water decomposes it similarly to the ortho-compound. Both the above chlorides are converted by aqueous sodium carbonate into monotolylarsenoxides, $AsO.C_7H_7$. These are white powders, resembling arsenious oxide, easily soluble in hot alcohol, insoluble in ether.

The ortho-compound fuses at 146°, the para-compound at 156°. On raising the temperature, both undergo decomposition, with liberation of arsenious anhydride, the latter yielding tritolylarsine, crystallising in plates (m. p. 129—130°).

Orthomonotolylarsenic acid, $C_7H_7.AsO(OH)_2$, is the product of the action of water on the tetrachloride previously mentioned. It crystallises from its aqueous solution in slender needles, which melt at 160° to a colourless liquid. The para-compound, similarly prepared, crystallises from its aqueous solution in long needles, which on heating do not melt, but are decomposed at a temperature of 300°.

C. F. C.

Diphenylbenzenes. By H. Schmidt and G. Schultz (*Deut. Chem. Ges. Ber.*, **11**, 1755—1756).—*Trinitroparadiphenylbenzene*, $C_{18}H_{11}N_3O_6$, formed by the action of fuming nitric acid on paradiphenylbenzene (m. p. 205°), crystallises from glacial acetic acid in long white needles (m. p. 190°). It is not oxidised by chromic acid. The dinitrodiphenylbenzene (m. p. 264°) is formed by nitrating a solution of paradiphenylbenzene in glacial acetic acid. This nitro-product forms yellow needles, insoluble in the ordinary solvents.

A solution of *isodiphenylbenzene* in glacial acetic acid yields, on oxidation with chromic acid, benzoic acid and a small quantity of diphenylcarbonic acid (m. p. 160°). W. C. W.

Diphenylene-methane. By R. Fittig and A. Schmitz (*Liebig's Annalen*, **193**, 134—142).—The authors find that the diphenylene-methane, $C_{13}H_{10}$, previously obtained by the former (*Ber.*, **6**, 187) from diphenylene-ketone on distillation with zinc-dust is identical with the fluorene discovered by Berthelot in coal tar (*Ann. Chim. Phys.* [4], **12**, 222), and more fully described by Barbier (*ibid.* [5], **7**, 479).

Diphenylene-methane picrate, $C_{13}H_{10} + C_6H_3(NO_2)_3O$, forms reddish-brown compact prisms (m. p. 80°).

Dibromodiphenylene-methane, $C_{13}H_8Br_2$, is obtained by adding gradually 2 mols. of bromine to 1 mol. of the hydrocarbon dissolved in carbon bisulphide. It forms beautiful transparent colourless tabular prisms (m. p. 162°). It is dimorphous, one of the forms being produced when a very small quantity of impurity is present.

Dinitrodiphenylene-methane, $C_{13}H_8(NO_2)_2$, is obtained on pouring the hydrocarbon into a mixture of equal volumes of fuming nitric acid and glacial acetic acid. It crystallises from boiling glacial acetic acid in colourless needles (m. p. 200°), which are very difficultly soluble in boiling alcohol.

On oxidation with chromic acid, diphenylene-methane is converted into diphenylene-ketone, no ketone corresponding to diphenylene-methane being produced. T. C.

Diphenylene Ketone and Phenylbenzoic Acid. By A. Schmitz (*Liebig's Annalen*, **193**, 115—128).—Diphenylene ketone, on oxidation with potassium chromate and sulphuric acid, is almost completely converted into carbonic acid and water, only a small quantity of benzoic acid being simultaneously produced.

Phenylbenzoic acid, $C_{13}H_{10}O_2$, is obtained when diphenylene ketone is fused with potash. It is insoluble in cold and difficultly soluble in hot water, but easily soluble in alcohol, from which it crystallises in small needles (m. p. 110°).

Barium phenylbenzoate, $(C_{13}H_9O_2)_2Ba + H_2O$, is equally soluble in hot and cold water, and easily forms supersaturated solutions. *Calcium phenylbenzoate* has the formula $(C_{13}H_9O_2)_2Ca + 2H_2O$. *Potassium phenylbenzoate*, $C_{13}H_9O_2K + H_2O$, crystallises in small brilliant prisms, which are easily soluble in water, but almost insoluble in concentrated potash solution. *Silver phenylbenzoate*, $C_{13}H_9O_2.Ag$, crystallises from hot water in needles, which darken slightly on exposure to light. *Ethyl phenylbenzoate*, $C_{13}H_9O_2.C_2H_5$, is a thick colourless oil (b. p. 300—305°), which does not solidify at −20°, and is insoluble in water, but easily soluble in alcohol and ether.

Nitrophenylbenzoic acid, $C_{12}H_8(NO_2).COOH$, is obtained by pouring phenylbenzoic acid gradually into fuming nitric acid, and is purified by means of the barium salt. It crystallises in colourless monoclinic crystals (m. p. 222°), which are almost insoluble in water, but easily soluble in hot alcohol. *Barium nitrophenylbenzoate*, $[C_{13}H_8(NO_2)O_2]_2Ba$ is easily soluble in water, and separates therefrom in warty crystalline masses. *Calcium nitrophenylbenzoate*, $[C_{13}H_8(NO_2)O_2]_2Ca$, resembles the barium salt.

Phenylbenzoic acid is not attacked on heating with dilute nitric acid or dilute potassium permanganate, but sulphuric acid and potassium

chromate oxidise it completely to carbonic anhydride and water. By fusion with potash it gives diphenyl and carbonic anhydride.

Details are given of the method of preparation of phenanthrenequinone from crude phenanthrene by oxidation with chromic mixture, and its conversion into diphenylene ketone by distillation with caustic lime. T. C.

Diphenic Acid. By J. Hummel (*Liebig's Annalen*, **193**, 128—134).—By the action of chromic mixture, diphenic acid is completely oxidised to carbonic anhydride and water; neither nitric acid nor potassium permanganate has any action.

Ethyl diphenate, $COOC_2H_5.C_6H_4.C_6H_4.COOC_2H_5$, crystallises in colourless brilliant cubes (m. p. 42°); it has, however, a great tendency to separate from its solutions as an oil.

Dinitro-diphenic acid, $C_{12}H_6(NO_2)_2(COOH)_2 + H_2O$, is obtained by the action of fuming nitric acid on diphenic acid, and is purified by means of the barium salt. It crystallises in long yellow needles, which give off their water of crystallisation at 150—160°, and melt at 248°. It is difficultly soluble in cold, but pretty easily soluble in boiling water, and easily in alcohol. *Barium dinitrodiphenate*, $C_{14}H_6(NO_2)_2O_4Ba + 6H_2O$, crystallises in clusters of needles, which are difficultly soluble in cold, but easily soluble in hot water.

Diamido-diphenic acid, $C_{12}H_6(NH_2)_2(COOH)_2$, is obtained by reduction of the dinitro-acid with tin and hydrochloric acid. The hydrochloride is easily soluble in water and but difficultly soluble in hydrochloric acid, from which it crystallises in colourless fatty-looking plates, decomposing at 100°. The free amido-acid is almost insoluble in hot water and in alcohol; it melts at 250°, and is identical with the acid obtained by Struve (*Ber.*, **10**, 75) from phenanthrenequinone. T. C.

Naphthalene Derivatives. By R. Meldola (*Deut. Chem. Ges. Ber.*, **11**, 1904—1907).—The author prepares bromacetonaphthalide by the action of bromine upon acetonaphthalide, dissolved in seven times its weight of glacial acetic acid, by which method he obtains 74 per cent. of the theoretical yield. By similarly brominating this body, he obtains dibromacetonaphthalide, crystallising in white silky needles (m. p. 225°), and easily soluble in alcohol, chloroform, and glacial acetic acid. The analogy between the preparation of this compound and [1 : 2 : 4] dibromamidobenzene (*Gazzetta chimica italiana*, 1874, 327) suggests a similar constitution. The author is investigating this point. C. F. C.

Fluoranthene, a New Hydrocarbon from Coal Tar. By R. Fittig and F. Gebhard (*Liebig's Annalen*, **193**, 142—160).—*Fluoranthene*, $C_{15}H_{10}$, was obtained from a large quantity of solid coal tar hydrocarbons of melting point near that of phenanthrene, but boiling at a much higher temperature. The hydrocarbon is extracted from admixed pyrene by means of the picric acid compound, which is somewhat more soluble in alcohol than the compound of pyrene and picric acid.

The empirical formula of the new hydrocarbon is intermediate between those of phenanthrene and pyrene. It is difficultly soluble in cold alcohol, but easily soluble in boiling alcohol, ether, carbon bisulphide, and glacial acetic acid. It separates in long needles from the concentrated alcoholic solution, but from very dilute solutions in large colourless plates (m. p. 109°).

Fluoranthene-picric acid, $C_{15}H_{10} + C_6H_3(NO_2)_3O$, crystallises in reddish-yellow needles (m. p. 182°), which are difficultly soluble in cold alcohol, but more easily in hot. It is decomposed on boiling with water.

Dibromofluoranthene, $C_{15}H_8Br_2$, is obtained when an excess of bromine is gradually added to a cold solution of the hydrocarbon in carbon bisulphide. It crystallises in brilliant yellowish-green needles (m. p. 204°); is very difficultly soluble in alcohol, ether, glacial acetic acid, and cold carbon bisulphide, but more easily soluble in the hot bisulphide.

Trinitrofluoranthene, $C_{15}H_7(NO_2)_3$, is obtained on adding the hydrocarbon gradually to fuming nitric acid. It crystallises from hot nitric acid, in which it is moderately soluble, in yellow needles, which do not melt at 300°. It is but little soluble in any of the ordinary solvents.

On oxidation with chromic acid or chromic mixture, fluoranthene yields a quinone and an acid, which are easily separated by treatment with sodium carbonate.

Fluoranthene-quinone crystallises from alcohol in small red needles (m. p. 188°), which are moderately soluble in alcohol and glacial acetic acid.

Diphenyleneketone-carbonic acid, $C_{14}H_8O_3$, is purified by means of the barium salt. It is almost insoluble in cold water, difficultly soluble in hot, and easily in alcohol and ether. It crystallises in orange-red needles (m. p. 192°), and is a monobasic acid.

The *barium salt* $(C_{14}H_7O_3)_2Ba + 4H_2O$, is somewhat difficultly soluble, but more soluble in hot than in cold water, and crystallises therefrom in fine silky needles. The *calcium salt* $(C_{14}H_7O_3)_2Ca + 2H_2O$, is equally soluble in hot and cold water. The *silver salt* is a yellowish green precipitate very little soluble in water. Diphenyleneketone-carbonic acid is converted into diphenylene-methane, when heated with zinc-dust, thus: $C_{14}H_8O_3 + 4H = C_{13}H_{10} + CO_2 + H_2O$. When heated alone or with lime, it gives diphenyleneketone, in the latter case accompanied by other products, thus: $C_{14}H_8O_3 = C_{13}H_8O + CO_2$. These facts prove the acid to have the constitution, $C_6H_4 \begin{matrix} CO \\ \diagup \\ \diagdown \end{matrix} C_6H_3.COOH$.

Isodiphenic acid, $C_{12}H_8(COOH)_2$, is obtained when the preceding acid is fused with potash, thus: $C_{12}H_7(CO).COOH + 2KHO = COOK.C_6H_4.C_6H_4.COOK + H_2O$.

It crystallises in small colourless needles (m. p. 216°), which are almost insoluble in water, but easily soluble in alcohol. *Barium isodiphenate*, $C_{14}H_8O_4Ba + 6H_2O$, is easily soluble in water, and crystallises in prisms. It loses 5 molecules of water at 130°, and the 6th at 190—200°. It does not deliquesce in the air. *Calcium isodiphenate*,

$C_{14}H_8O_4Ca + 2H_2O$, is almost insoluble in water. *Silver isodiphenate*, $C_{14}H_8O_4Ag_2$, is but little soluble in boiling water.

Isodiphenic acid is isomeric and not identical with the two known diphenylcarbonic acids or with the acid obtained by Carnelley (this Journal, 1877, **2**, 653) by the oxidation of ditolyl. When heated with lime it yields diphenyleneketone.

The authors ascribe the following constitution to fluoranthene :—

$$\begin{array}{l} C_6H_4.CH.CH \\ \quad | \quad / \quad \| \quad . \\ C_6H_3\text{——}CH \end{array}$$

T. C.

Idrialin. By G. Goldschmidt (*Deut. Chem. Ges. Ber.*, **11**, 1578—1581).—The author has examined idrialin, the substance occurring in the mercury ores of Idria, and has obtained analytical results which agree with those of Laurent, Dumas, and Bödecker ; therefore proving idrialin not to be a hydrocarbon as Schrötter and others have stated. The formula for idrialin is more probably $C_{40}H_{28}O$ than $C_{42}H_{28}O$, as Bödecker would represent it.

Idrialin can be obtained from the mineral either by distillation in a stream of hydrogen or carbon dioxide, or by extracting it by means of amyl alcohol, turpentine oil, or xylene. It is best purified by recrystallisation from xylene. The statement of Dumas that idrialin cannot be distilled without decomposition can apply under certain conditions only, as no appreciable loss occurs (only a small carbonaceous residue) when the pure substance is distilled as above directed.

Bromine-compounds.—Two bromine compounds have been obtained ; the one, $C_{40}H_{22}Br_6O$, is produced by adding bromine to a solution of idrialin in boiling glacial acetic acid ; the other, $C_{40}H_{19}Br_9O$, by adding bromine to idrialin under water.

Oxidation-products.—A red compound of the formula, $C_{40}H_{20}O_5$, of indistinct crystalline character, in addition to a resinous body which readily dissolves in alcohol, is formed by acting on idrialin with a solution of chromic acid in glacial acetic acid. It yields idrialin by distillation over zinc-dust, and forms a beautiful violet colour with concentrated sulphuric acid. When heated in a stream of hydrogen, there distils over at a temperature of about 280° an almost colourless oil, which finally solidifies to a crystalline mass ; it corresponds in composition and properties with stearic acid. The residue in the retort consists of a black shining mass, which is still under investigation. Among the products of oxidation, the author has also obtained a body which is difficultly soluble in spirit, and gives an emerald-green colour with sulphuric acid. It has the same percentage composition as the one above described, but whether it similarly yields stearic acid has not yet been ascertained. A. J. C.

Structure of Terpenes. By F. Flavitzky (*Bull. Soc. Chim.* [2], **30**, 434).—The author denies that in these bodies the carbon atoms are grouped as in the aromatic bodies, and proposes for camphor the following formula $(CH_3)_2CH.CH(CH_3).CH{=}CH.CH{=}CH.CHO$. To the camphenes which possess rotatory power he gives the formula, $(CH_3)_2CH.CH(CH_3).CH{=}CH.CH{=}C{=}CH_2$, which satisfies Van't Hoff's law concerning the asymetric carbon atom.

n 2

The formula for turpentine and australene he writes as follows: $(CH_3)_2CH.CH(CH_3).CH{=}CH.C{\equiv}C.CH_3$.

The optically inactive modifications of these bodies he expresses by the following formulæ: $(CH_3)_2C{=}C(CH_3).CH_2.CH_2.C{\equiv}C.CH_3$, or $(CH_3)_2C{=}C(CH_3).CH_2.CH_2.CH{=}C{=}CH_2$. L. T. O'S.

Dextrogyrate Russian Terpene from the Turpentine of Pinus Silvestris. By F. Flavitzky (*Bull. Soc. Chim.*, **30** [2], 433).—This terpene, which the author considers to be identical with that obtained by Attersberg from the tar of the Swedish *Pinus sylvestris* (*Bull. Soc. Chim.*, **30**, 191), has a sp. gr. 0·8746 at 0°, and boils between 155·5—156·5°, its rotatory power is $[\alpha]_D = +27{\cdot}7$. When treated with hydrochloric acid, it yields a crystalline monochlorhydrate, which melts at 127°, and boils at 204°, slightly decomposing at the same time; its rotatory power is $[\alpha]_D = 14{\cdot}7$. L. T. O'S.

Camphene from Camphor, and its Homologues. By F. V. Spitzer (*Deut. Chem. Ges. Ber.*, **11**, 1815—1818).—By the action of sodium on an ethereal solution of camphor dichloride (m. p. 155°), a crystalline camphene is produced, which melts at 57·5—58·8°, and boils at 159·9°. It combines with hydrochloric acid to form $C_{10}H_{16}HCl$.

Ethyl-camphene, $C_{10}H_{15}.C_2H_5$, obtained by treating a mixture of camphor chloride and ethyl iodide with sodium, is a colourless mobile liquid, which boils at 198—199·9°.

Isobutyl-camphene, $C_{10}H_{15}.C_4H_9$, is a colourless liquid, resembling turpentine in smell. It boils at 228—229°, and has a sp. gr. of 0·8614 at 20°.

These three camphenes are dextrogyrate. W. C. W.

Camphor Dichloride. By F. V. Spitzer (*Deut. Chem. Ges. Ber.*, **11**, 1818—1820).—Camphor dichloride, $C_{10}H_{16}Cl_2$, is obtained by adding camphor (1 molecule) in small quantities at a time, to well cooled phosphorus pentachloride ($1\frac{1}{3}$ molecules), and leaving the mixture at rest for 14 days. The oily liquid which separates out is poured into water, when it solidifies to a white mass. Camphor dichloride is deposited from an ethereal or alcoholic solution in white or colourless needle-shaped crystals, which melt at 155°. The solution in ethyl acetate deviates the plane of polarised light to the left.

W. C. W.

Cinchona Alkaloïds. By A. Claus (*Deut. Chem. Ges. Ber.*, **11**, 1820—1825).—Homocinchonidine, $C_{19}H_{22}N_2O$, unites with ethyl iodide to form a crystalline compound, which melts at 261° with decomposition, and is soluble in hot water and in alcohol, but is insoluble in ether. By the action of silver oxide on this substance a base is obtained, which forms a platinum double chloride having the composition, $C_{19}H_{22}N_2O.C_2H_5Cl.HCl.PtCl_4.H_2O$. On the addition of an acid to the ethyl iodide compound, the following reaction takes place:

$$3C_{19}H_{22}N_2O.C_2H_5I + H_2SO_4 = C_{19}H_{22}N_2OC_2H_5I.I_2 + (C_{19}H_{22}N_2OC_2H_5)_2SO_4 + H_2.$$

Ethyl-homochonidine, $C_{21}H_{26}N_2O$, obtained by boiling homocinchonidine-ethiodide with potash and extracting the product with ether, crystallises in glistening needles (m. p. 91°), which are insoluble in water, but dissolve readily in alcohol, ether, benzene, and chloroform. Ethyl-homocinchonidine forms a crystalline addition product (m. p. 236°) with ethyl iodide, and a double salt with platinum chloride, $C_{21}H_{26}N_2O.2HCl.PtCl_4.H.O$.

The ethyl iodide compounds with all the cinchona alkaloïds, resemble homocinchonidine-ethiodide in their decomposition by potash. Compounds of cinchona bases with 2 molecules of ethyl iodide can be obtained by heating the base with an excess of the iodide. *Homocinchonidine-diethiodide*, $C_{19}H_{22}N_2O2C_2H_5I + H_2O$, forms transparent golden-yellow crystals, which melt at 255° with decomposition, and *cinchonine-diethiodide* is deposited from an aqueous solution in amber-coloured crystals.

Both these compounds are deprived of their iodine by silver oxide, and yield alkaline solutions.

The author remarks that the iodides of compound ammonias containing aromatic or unsaturated radicles are decomposed by potash.

W. C. W.

A New Quinine Salt. By Drygin (*Chem. Centr.*, 1878, 622).—One equivalent of quinine hydrochloride is dissolved in one equivalent of hydrochloric acid (sp. gr. 1·09), the solution is filtered, one equivalent of pure urea is added, and after solution (which is aided by gently warming) the liquid is allowed to crystallise. The crystals are washed with a very small quantity of cold water, and dried at a moderate temperature. By evaporating the mother-liquor a fresh crop of crystals may be obtained. The new salt, for which no formula is given, but which the author calls by the barbarous name of *quininum dimuriaticum carbamidatum*, crystallises in hard four-sided prisms; at ordinary temperatures it dissolves in its own weight of water with production of cold. The crystals are not hygroscopic; they melt at 70—75°, forming a yellow liquid. The salt is soluble in alcohol, but is reprecipitated by ether, probably after undergoing partial decomposition.

M. M. P. M.

Cinchonichine, a New Quinine Alkaloïd. By Drygin (*Chem. Centr.*, 1878, 622).—The brown mother-liquor from the last crystals of the quinine salt described above (see preceding abstract) is saturated with ammonia, the precipitate is washed, dried, treated with ether, dissolved in a little chloroform, and after filtering off the undissolved cinchonidine, is allowed to crystallise. The crystals are converted into sulphate, and this salt, after purification by crystallisation, is again decomposed by ammonia, when a new alkaloïd, called by the author *cinchonichine*, is obtained. The properties of the new body seem to place it midway between the quinine and cinchonine groups of alkaloïds. No analyses are given.

M. M. P. M.

Bark of the Root of the Pomegranate. By Durand (*J. Pharm. Chim.* [4], **28**, 168—170).—The dried bark, which has been kept for 12 months, is powdered and exhausted first with ether, which dis-

solves the chlorophyll, and then with alcohol of 95°, which dissolves out a yellowish-brown resin. The residue is dried and mixed with milk of lime, the mixture dried and heated with alcohol of 95°. The alcoholic solution is evaporated to a small bulk, and after being filtered is treated with ammonia, when a light white deposit forms; this is extracted with chloroform, and on evaporating the extract, a yellowish-brown residue is obtained, having an alkaline reaction. The residue when dissolved in acetic acid gave a white precipitate with Mayer's reagent, and a brownish-yellow coloration when treated with iodine solution; it is therefore an alkaloïd. It may be obtained crystalline by dissolving the residue in sulphuric acid, after removing the chloroform, evaporating the resulting solution to dryness, dissolving the residue in water, and adding ammonia; the solution is then shaken with chloroform, which on evaporation leaves a white crystalline residue. The author has prepared the hydrochloride, but not studied its properties. He proposes to call the alkaloïd *granatine*.

L. T. O'S.

Pelletierine, a Base from the Bark of Pomegranate. By C. Tanret (*J. Pharm. Chim.* [4], **28**, 384—386).—This body, which has been described (*Chem. Soc. J.*, **34**, 739), may be prepared in a state of purity by distilling its ethereal solution in a current of hydrogen; the residue is kept at a temperature from 130—140°, until water is no longer given off, when the temperature is raised to 180—186° and the alkaloïd begins to distil. It is thus obtained as a colourless liquid, which quickly changes colour in the air. Its sp. gr. is 0·999 at 0° and 0·985 at 21°. It dissolves in water, contraction taking place; a mixture of 1 part of pelletierine and 2·5 parts of water having a sp. gr. = 1·021 at 21°. The alkaloïd is dextrogyrate, its power of rotation $[\alpha]_j = +8$, and that of the sulphate + 5·9. With potassium dichromate and sulphuric acid pelletierine gives an intense green coloration.

According to its analysis and those of its salts, its formula is $C_{16}H_{13}NO_2$. It is a mon-acid base, and forms a hydrochloride, $C_{16}H_{13}NO_2.HCl$, and a sulphate, $C_{16}H_{13}NO_2.HSO_4$. The vapour density of the base also corresponds to the above formula.

The author has sought to determine the amount of alkaloïd in the different species of pomegranate, and also the influence of growth on its formation. He gives tables showing the numbers obtained.

According to the observations of several medical men in Troyes and Paris, pelletierine is the tænicide principle of pomegranate.

L. T. O'S.

Urobilin. By L. Disqué (*Chem. Centr.*, 1878, 711).—Urobilin occurs in pathological urine; fresh normal urine contains a colourless body which may be produced artificially by reducing urobilin, and which again passes into the latter compound by taking up oxygen from the air; this action is especially marked in presence of acids or of chloroform. M. M. P. M.

Iron Albuminates. By E. Holdermann (*Arch. Pharm.* [3], **13**, 149—160).—The term "iron albuminate" is given to compounds produced by the addition of an iron salt to albumin. These appear to be

indefinite in composition, and no one up to the present time has been able to answer the questions: What are the conditions under which the albuminate is precipitated? If the precipitate is of a definite constitution, by what means may it be isolated? What influence has the acid of the iron salt upon the composition of the albuminates? The author has prepared albuminates from several ferric salts, and dried them at 40°, some being washed with water, others being dried unwashed. The washing appears to have but little influence on the substance, judging by the ash left on ignition. The precipitate produced by the addition of ferric chloride to albumin is soluble in excess of the chloride, and the precipitate produced by the addition of albumin to ferric chloride is soluble in a very large excess of the albumin. If the alkalinity of the albumin be neutralised by hydrochloric acid, no precipitate is produced with ferric chloride; but if on the contrary the alkalinity be increased by the addition of potash, a copious precipitate is immediately produced, which is soluble in excess of the alkaline albumin. Acidifying and neutralising the ferric chloride produce similar effects, with the exception that the neutral ferric chloride does not, when in excess, dissolve the precipitate. The precipitates were analysed by ignition, and the iron determined in the ash; the conclusions arrived at are, that the acidity or alkalinity has an influence on the formation of the albuminate; that the albuminates have a definite composition which is not altered by washing; that the nature of the acid combined with the iron has great influence on the composition of the albuminates; the albuminates produced from salts of iron whose acid is not combustible or volatile, as sulphuric acid, have a larger proportion of iron present than those from iron salts of volatile acids, as hydrochloride or citric acids, also that basic ferric salts cause a compound to be formed having a larger percentage of iron than neutral or acid salts. E. W. P.

Crystalline Structure in Bees'-Wax. By Böttger (*Chem. Centr.*, 1875, 575).—Bees'-wax may be obtained in a well-defined crystalline form by fusing it on the surface of hot water, and allowing it to cool very slowly. M. M. P. M.

Constituents of Hops. By G. Kuhnemann (*Chem. Centr.*, 1875, 573).—The oil obtained by distilling hops in a current of steam is a complex mixture containing hydrocarbons, oxidised bodies, &c. The addition of dilute acids to the oil distilled from sulphured hops causes an evolution of sulphuretted hydrogen; such hops can be distinguished from unsulphured hops by this reaction.

The nonvolatile portion of hops consists of various carbohydrates, rosins, colouring matters, tannin, nitrogenous bodies, and a hydrocarbon crystallising at low temperatures. M. M. P. M.

Colouring Matter of Red Wine. By J. Erdmann (*Deut. Chem. Ges. Ber.*, **11**, 1870—1876).—The object of this investigation is to establish a more certain basis for the examination of red wines, in an accurate knowledge of the properties and reaction of the bodies to which they owe their colour. The author found that the Bordeaux

wine ("Chat. Cantenac Brown") which he took as his subject, gave on neutralisation with ammonia the usual bottle-green coloration; but that if a few drops of concentrated hydrochloric acid be previously added, a fine greenish dark-blue colour was obtained. This he regards as due to the colouring matter being resolved into two others, separable by agitating the wine (after the addition of hydrochloric acid) with amyl alcohol; this menstruum dissolves and removes the body, which gives the characteristic green coloration with ammonia, forming a red-violet solution, leaving the aqueous solution coloured yellowish-red, but giving with ammonia an indigo-blue coloration which persists for some minutes and then passes through various shades of blue to a brownish-green. These observations were made with a new wine; the author has extended them to the wines of the same brand for a series of years; his results are tabulated so as to admit of a ready differential comparison. It will be seen that the colouring matter undergoes a gradual change. C. F. C.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Salicylic Acid, Thymol, and some Essential Oils on Germination. By E. Heckel (*Compt. rend.*, **87**, 613—614). The author finds that by acting on 100 seeds of various mono- and di-cotyledons with ·025 gram of pure phenol, germination is suspended. With a solution of salicylic acid made by mixing ·05 gram mixed with 50 c.c. of water, germination in the same number of seeds is prevented. Phenol merely suspends germination, the latter action proceeding when the phenol has evaporated; salicylic acid prevents it altogether. Salicylate of soda acts like salicylic acid, but although soluble in water, its action does not appear to be more rapid. Crystallised thymol has an action comparable with that of phenol and salicylic acid. It suspends germination, and arrests it altogether in certain cases. On about 100 seeds ·025 gram acts with energy, although it is only slightly soluble. The essential oils of thyme and of rosemary as well as turpentine oil also prevent germination even when used in very small quantities. C. E. C.

Fungoïd Fermentations. By A. Fitz (*Deut. Chem. Ges. Ber.*, **11**, 1890, 99).—The author continues his investigation of the mode of resolution of various compounds under the influence of fungoïd ferments. *Erythrite* (2 mols.) subjected to the action of a mixed ferment, developed from cow-dung, was resolved into butyric acid (1 mol.) and succinic acid (1 mol.), with elimination of water and hydrogen.

Glycerin was decomposed under the influence of the following ferments. (1.) *Bacillus subtilis* obtained from hay. The chief product was ethyl alcohol, in amount equal to 25·7, 25·8, and 29·0 p.c. of the glycerin in three several experiments. (2.) *Blue Pus.*—From 100 grams glycerin decomposed by the fungus of blue pus were obtained: 10·9 grams of crude alcohol (anhydrous) chiefly ethyl, but containing also a liquid

(0·8 gram) boiling at 114—117°; 9·0 grams of calcium salts of volatile acids, which proved to be butyric with a small quantity of acetic; and also 0·71 gram succinic acid. This is the first observation of the formation of succinic acid in glycerin fermentation. (3.) *Yellow Pus.*—In all cases blue colouring matter was formed. (4.) *Orange Pus.*—The fermentation induced by the fungus from orange pus was very rapid; 100 grams glycerin yielded 23·89 of nearly pure ethyl alcohol; traces only of acids were formed; calcium lactate and malate are indifferent towards this ferment. (5.) *Ordinary Pus.*—The fungus from this substance induced a slow fermentation, which is still under investigation. (6.) Fermentation of 1½ p.c. glycerin solution by a *Micrococcus* mixed with a *Bacillus*. The process occupied four weeks, 50 grams glycerine yielded 15·65 grams crude alcohol (anhydrous), chiefly ethyl; 8·5 grams of a mixture of calcium butyrate, acetate, and formate. No non-volatile acids were formed. The decomposition of glycerin by this fermentation is very complete, probably by reason of the excessive dilution of the liquid preventing the accumulation of alcohol in quantity sufficient to impair the activity of the fungus.

Mannite was decomposed under the fermentation induced by a *Bacillus* (club-shaped); 100 grams yielding 26·3 grams ethyl alcohol; 7·9 grams of calcium salts of volatile acids, chiefly formic, and 0·04 gram succinic acid.

Calcium Citrate.—The fermentation was that of a slender *Bacillus*, and occupied 13 days, 100·6 grams of the anhydrous acid yielded 4·759 alcohol, which was found to be ethyl and not isopropyl alcohol, as might perhaps have been expected, 72·9 grams of pure calcium acetate, and 0·41 grams succinic acid.

Calcium Malate undergoes three several decompositions under the influence of respective ferments, viz.:

(1.) *Succinic Acid Fermentation.*—Induced by a body in the form of minute rods. No alcohol was formed; 19·9 grams calcium salts of volatile acids, which proved to be pure acetate, were obtained; and also 62·23 grams succinic acid. These quantities closely satisfy the equation $3C_2H_3(OH)(COOH)_2 = 2C_2H_4(COOH)_2 + C_2H_4O_2 + 2CO_2 + H_2O$.

(2.) *Propionic Acid Fermentation.*—Through the agency of a short cylindrical *Bacillus*, 53·6 grams malic acid yielded 0·5 gram alcohol; 29·6 grams calcium salts of volatile acids, viz.: about 18 grams propionic and 6 grams acetic acid, and 0·07 gram succinic acid. The decomposition is approximately that represented by the equation: $3C_2H_3(OH)(COOH)_2 = 2C_3H_6O_2 + C_2H_4O_2 + 4CO_2 + H_2O$.

(3.) *Butyric Acid Fermentation.*—This is at times induced under the same conditions as and takes the place of the succinic acid fermention of calcium malate. It is probably due to a specific ferment, and not to any variation in the temperature of the reaction or the quantities of material employed. It is explained by the following equation: $2C_2H_3(OH)(COOH)_2 = C_4H_8O_2 + 4CO_2 + 2H_2O$.

Calcic Lactate.—In addition to the butyric, previously investigated, a propionic fermentation of this compound is induced by a long slender *Bacillus*, 3 mols. lactic acid, yielding 2 mols. propionic and 1 mol. acetic acid, with elimination of 1 mol. CO_2 and 1 mol. H_2O.

C. F. C.

Ripening of Grapes. By B. Haas (*Chem. Centr.*, 1878, 700).—A résumé of the state of knowledge on this subject (see this Journal for 1875, p. 281, and 1873, p. 402). The theories of Liebig, Sachs, and Neubaer, as to the origin of sugar in the grape, &c., are discussed. M. M. P. M.

Origin of Chlorophyll Corpuscles. By C. Mikosch (*Chem. Centr.*, 1878, 681).—In young organs, which afterwards become green, the starch-granules have a direct influence on the production of chlorophyll. Each starch-granule surrounds itself with a layer of plasma, which gradually becomes more and more green as the starch disappears. If the plant be kept in the dark a similar change takes place, but the colourless etiolin corpuscles produced do not become green on removing the plant into the light, provided the starch has wholly disappeared. In those parts of the plant which are devoid of starch, chlorophyll is formed from hyaline plasma in the manner described by Sachs.
M. M. P. M.

Composition of the Growing Potato. By C. Kellermann (*Chem. Centr.*, 1878, 604—605).—Analyses were made weekly of growing potatoes. The constituents of the seed tubers, taken as a whole, showed an increase from week to week, but relatively a decrease in the nitrogenous extractive matter. Cellulose formed an exception to this rule, the amount fluctuated within somewhat wide limits. The amount of lime regularly increased, being nearly six times as much in the fourteenth week as during the first week. The lime is present in the older tubers in the form of calcium oxalate.

The proteïds decrease in the stems and leaves as the plant grows; the non-nitrogenous extractive matter decreases continuously in the leaves; the ash increases in both leaves and stems until the eighth week, after which it decreases.

Potash and lime reach their relative maxima in the stems during the eighth week, phosphoric acid during the fifth week. Cellulose is present in largest amount in the stems between the ninth and fourteenth weeks.

The main production of organic compounds occurs in the young tubers from the ninth to the fourteenth week, but during this period the amount of the proteïds in the stems and leaves decreases from the ninth week.

The intensity of the assimilative process increases regularly.

Various details, but very few quantitative data, are given in the original paper. M. M. P. M.

Physiological Chemistry.

Action of Carbonic Anhydride on the Animal Organism. By C. Friedlander and E. Herter (*Chem. Centr.*, 1878, 682).—If administered in small hourly doses, carbonic anhydride causes increased action of the heart, and increased rapidity of breathing. When a gas

containing about 30 per cent. of carbonic anhydride is inhaled depression quickly succeeds the first symptoms; the heart beats more slowly, the breathing becomes slow and laboured, the temperature rapidly falls, the blood pressure is lessened, and death finally ensues. The poison appears to attack the central apparatus of the nervous system.

M. M. P. M.

Researches on the Urea contained in the Organs. By P. Picard (*Compt. rend.*, **87**, 533—535).—Solutions obtained by boiling equal weights of finely-chopped muscle, brain, and liver, with water and sulphate of soda, after filtration, are treated with sodic hypobromite, according to a method previously described by the author. By measuring the volumes of the gases evolved, the comparative quantities of urea contained in equal weights of muscle, brain, and liver, can be ascertained. It is found, firstly, that with the organs of an animal killed whilst fasting, and whose stomach is empty, the volumes of gas evolved from equal weights of muscle, brain, and liver, are greater with the first than with the second, and greater with the second than with the last of these organs. With the organs of an animal killed in full process of digestion there is found to be a considerable increase in the quantity of urea in the liver, whereas there is but very little augmentation in the muscles and the brain; in fact in the latter organs the increase is probably only apparent. In order to appreciate the foregoing facts, it is needful to remember that the amount of urea in the blood of a digesting animal is greater than in that of a fasting one. The author concludes that, during digestion, urea is formed in the muscles, the brain, and the liver; that these organs all contain a greater amount of urea than do equal weights of blood, and that during fasting, urea seems to be formed solely in the brain and muscles. These conclusions are formed on the supposition that the nitrogen disengaged by the hypobromite is all due to decomposition of urea; but even if this be not true, the variations in the composition of the blood, liver, &c., are facts that still remain. The author adds that he has obtained from muscle a solution which gives the reactions of urea.

C. E. C.

Albuminoïd-Compounds of the Organs, and of the Spleen in particular. By P. Picard (*Compt. rend.*, **87**, 606—608).—The contracted spleen of a dog macerated with water, and digested with it for some time, yields a liquid which contains two distinct albuminous substances besides hæmoglobin. The precipitate obtained by passing carbonic acid through this liquid to saturation, is washed with carbonic-acid water, and having been re-dissolved in aërated water, gives the ordinary reactions of a globulin. Another albuminoïd exists in the liquid from which the globulin has been precipitated, and may be thrown down by heating to a temperature of about 75°. That globulin exists in the spleen independently of the presence of blood is shown by comparative experiments made with equal weights of the blood and spleen of the same dog conducted in the manner above described. A greater quantity of globulin is obtained from precipitation of about three-quarters of the spleen solution than from precipitation of the

whole of the blood solution. If the quantities of hæmoglobin in the two solutions be compared, there is found to be far less in the spleen solution than in the blood solution. C. E. C.

Occurrence and Origin of Hypoxanthine and Lactic Acid in the Animal Body. By G. Salomon (*Chem. Centr.*, 1878, 681).—Hypoxanthine is a normal constituent of human bone-marrow, and of various glandular organs; also of the blood of human subjects, and of dogs after death. The absence of this body in venous blood seems to show that the compounds therein produced are more quickly oxidised during life than after death. The presence of hypoxanthine is probably due to pancreatic fermentation of fibrin. Lactic acid is a normal constituent of the blood of human subjects, and is probably formed by the decomposition of carbohydrates in the blood; it is generally absent from venous blood. M. M. P. M.

Synthetic Processes in the Animal Body. By M. Jaffé (*Chem. Centr.*, 1878, 681).—It has been already shown by the author (this Journal, 1875, p. 478) that paranitrotoluene is oxidised within the organism partly to paranitrobenzoic and partly to paranitrohippuric acid. Orthonitrotoluene is in like manner partially oxidised to orthonitrobenzoic acid, but the main product of the oxidation consists of a new acid, called by the author *uronitrotoluic acid.*

The new acid has the empirical formula $C_{13}H_{15}NO_9$, and is regarded by its discoverer as a compound of nitrobenzyl alcohol with a hypothetical acid, $C_6H_{10}O_7$; thus $C_{13}H_{15}NO_9 + H_2O = C_6H_4NO_2.CH_2(OH) + C_6H_{10}O_7$.

Uronitrotoluic acid passes out of the system in combination with urea in the form of a compound, having the composition $C_{14}H_{19}N_3O_{10}$.

M. M. P. M.

Secretion from the Sebaceous Glands of Birds. By D. de Jonge (*Chem. Centr.*, 1878, 711).—This secretion (from geese and wild ducks) contains caseïn, albumin, nucleïn, lecithin, fatty acids, and a substance resembling cholesterin; potassium, sodium, calcium, magnesium, and chlorine are also present. Sugar and urea are absent. M. M. P. M.

Analytical Chemistry.

Application of Witt's Tropæolins to Titration. By G. Lunge (*Deut. Chem. Ges. Ber.*, **11**, 1944).—The author confirms the observations of W. v. Miller (*Ber.*, **11**, 460) on the use of Witt's tropæolin (00) in the titration of sodium carbonate, &c. He has further observed an equally sudden colour transition in the titration of sodium sulphide by hydrochloric acid in presence of this body. Several of the azo-colouring matters are similarly unaffected by carbonic and hydrosulphuric acids, but undergo a characteristic transformation

with the least excess of a mineral acid, and are therefore accurate indicators of the saturation of carbonates and sulphides; the author notices more especially Poirier's Orange III (dimethylaniline-diazobenzenesulphonate), diazo-α-naphtholsulphonic acid and amidobenzene. Of the latter it is remarkable that it is not destroyed by hydrogen sulphide in presence of excess of mineral acid. Witt's tropæolin 000 exhibits an inverse change of colour, viz., from yellow in acid to red in alkaline solutions, and is therefore an excellent indicator of the presence of free alkali or alkaline carbonate. The weaker acids, such as sulphurous and oxalic, induce a much less rapid and regular transition. Acetic acid is indifferent towards these bodies; sodium thiosulphate behaves like the salts of the stronger mineral acids, the smallest quantity of hydrochloric acid added to its solution in presence of tropælin causes an instant change of colour. It follows from the above that not only the purer products, but crude soda, &c., may be accurately titrated by means of these indicators. C. F. C.

Determination of Vapour Density. By V. Meyer (*Deut. Chem. Ges. Ber.*, **11**, 1867—1870).—The author describes the apparatus and method for determining the vapour densities of bodies that attack mercury or Wood's metal, by a process similar in principle to that recently published by A. W. Hoffmann (*Ber.*, **11**, 1684), but independently originated.

A glass tube of rather more than 100 c.c. capacity, closed at one end, is drawn out at the other to a tube of about one-seventh the original diameter (the length of this narrower portion being greater than that of the wider), terminating in an enlargement which admits an india-rubber cork, accurately adjusted to a mark on the tube. At a short distance below this mark an exit-tube leaves the narrow portion, at right angles, to pass, after being suitably bent, beneath the surface of mercury contained in a trough. Heat is applied to the lower portion of the apparatus by bringing it into the vapour of a liquid kept boiling in a second larger tube. When the air in the apparatus has reached a constant expansion at the temperature of the experiment, *i.e.*, when no more bubbles escape from the exit-tube, a graduated jar filled with water is brought over the mouth of the latter, the cork removed, the weighed substance introduced, and the cork rapidly replaced. The substance is quickly vaporised, the vapour expels equivalent volume of air by the exit-tube into the graduated jar; this is measured under ordinary conditions of pressure and temperature, and from this quantity, after correction, the required vapour density is at once known. This mode of measuring the volume of the vapour eliminates two prominent factors of determinations by the older methods, viz., the volume of the vessel in which the substance is vaporised, and the temperature under which its volume is observed.

The author gives the results of a number of determinations by this method, which shows that the two sources of error to which it is subject, viz., those due to diffusion and to the discrepancy between the volume of two mutual indifferent gases in contact, and the sum of their volumes when isolated, are without sensible influence.

C. F. C.

Application of Glycerin. By E. Donath (*Dingl. polyt. J.*, **229**, 542—544).—The property which glycerin possesses of dissolving certain metallic oxides and hydroxides, and of preventing the precipitation of others by fixed alkalis, has been known for some time. Puls has recently investigated and described some metallic glycerides, on the formation of which probably these appearances depend.

By experimenting in this direction, the author found that a mixture of glycerin and solution of caustic soda (sp. gr. 1·2) in equal volumes has the property of dissolving the higher oxides of certain metals. The precipitation of manganous oxide by fixed alkalis, for instance, is not prevented by glycerin; but if the precipitate is exposed to the air for a short time only, a deep cherry-red solution is formed. A similar result is obtained on treating the precipitate, formed by sodium hypochlorite and manganese solutions, with the above mixture. The precipitation of nickelous and cobaltous oxides by potash is also not prevented by glycerin; in the latter case a green solution containing cobalt is obtained owing to slow oxidation in the air. Mixtures of glycerin and caustic soda, or ammonia, possess distinct reducing properties.

The black nickel hydroxide obtained by heating solutions of nickel with sodium hypochlorite is reduced by glycerin and soda already in the cold; the cobaltic oxide produced in a similar manner being less readily reduced in the cold, but more readily on heating. When a mixture of glycerin and ammonia is used, to which a small quantity of sal-ammoniac solution is added, nickelous oxide dissolves, forming a blue solution, whilst only very small quantities of cobalt dissolve even after some time. This reaction may be employed to detect small quantities of nickel in presence of larger quantities of cobalt. The reaction of the glycerin soda solution with copper and cadmium oxides, the former being dissolved and not the latter, serves not merely for their detection, but may also be used for their accurate quantitative separation. For qualitative purposes the corresponding metallic sulphides are dissolved in dilute, warm nitric acid, and treated with glycerin and soda solution. If copper alone is present a blue solution is obtained, whilst in the presence of cadmium, insoluble cadmium hydroxide is simultaneously formed, which is filtered off, washed, and is easily recognised by conversion into the sulphide. To separate both metals quantitatively their solution is treated with an excess of glycerin soda solution in a platinum or porcelain dish, warmed for about 20 minutes on a water-bath; after which the separated cadmium oxide is filtered off, washed first with hot water containing glycerin soda solution, and finally with pure water: it is then dried and ignited, using the precautions necessary, owing to the volatility of the possibly reduced cadmium. The mass is then weighed as cadmium oxide. In the filtrate, copper may be precipitated by heating with grape sugar, igniting the precipitate, and weighing it as cupric oxide; or the filtrate may be treated with ammonium chloride, and titrated with potassium cyanide. The results are satisfactory in both cases. The precipitation of alumina and chromium oxide by ammonia is not in the least interfered with by the presence of glycerin as is the case with tartaric acid; as the solvent property of glycerin soda solution, in

respect of certain metallic hydroxides is greater than that of tartaric acid in the presence of free alkalis, the former may be used in many cases with advantage instead of tartaric acid, *e.g.*, in the separation of alumina, chromium, and iron oxides. D. B.

Reagent for Detecting Nickel. By R. Böttger (*Chem. Centr.*, 1878, 606).—An aqueous solution of potassium xanthate produces a yellow colour with very minute traces of nickel salts; a similar colour is also produced with copper salts, but it disappears on adding ammonia, whilst the coloration obtained with nickel does not; with larger quantities of nickel salts, a yellow precipitate is produced. M. M. P. M.

Valuation of Body Colours. By Reimann (*Chem. Centr.*, 1878, 606) —A standard colour is obtained from a known source, and a weighed amount of it is mixed with zinc-white until the colour is equal to that of the material to be tested. A second weighing gives the amount of zinc-white added, and from this, the relative value of the colour under examination may be estimated. White colouring matters are valued by mixing them with a standard black so as to produce a grey shade similar to that obtained by mixing an equal quantity of the standard black with a standard white taken for comparison. M. M. P. M.

Estimation of Alcohol and Extractive Matter in Wine. By H. Hager (*Chem. Centr.*, 1878, 415).—The sp. gr. of the wine is determined: 100 c.c. are evaporated to about $\frac{1}{3}$ the original volume, the residual liquid is diluted with water to 100 c.c., and the sp. gr. is again determined. The difference between the two numbers deducted from 1,000 gives the sp. gr. of dilute alcohol equal in strength to the original wine; from this, the amount of alcohol is found by the use of tables. From the second sp. gr. determination (that of the aqueous extract) the percentage amount of extractive matter may be found by the aid of the following table, which is based upon the author's experiments.

Temperature = 15°. The sp. gr. increases or diminishes by 0·00024 for each degree C.

Per cent. of extractive.	Sp. gr.	Per cent. of extractive.	Sp. gr.	Per cent. of extractive.	Sp. gr.
0·50	1·0022	4·00	1·0183	7·50	1·0343
0·75	1·0034	4·25	1·0194	7·75	1·0355
1·00	1·0046	4·50	1·0205	8·00	1·0367
1·25	1·0057	4·75	1·0216	8·25	1·0378
1·50	1·0068	5·00	1·0228	8·50	1·0390
1·75	1·0079	5·25	1·0239	8·75	1·0402
2·00	1·0091	5·50	1·0251	9·00	1·0414
2·25	1·0102	5·75	1·0263	9·25	1·0426
2·50	1·0114	6·00	1·0274	9·50	1·0437
2·75	1·0125	6·25	1·0286	9·75	1·0449
3·00	1·0137	6·50	1·0298	10·00	1·0461
3·25	1·0148	6·75	1·0309	10·25	1·0473
3·50	1·0160	7·00	1·0321	10·50	1·0485
3·75	1·0171	7·25	1·0332	10·75	1·0496

Per cent of extractive.	Sp. gr.	Per cent. of extractive.	Sp. gr.	Per cent. of extractive.	Sp. gr.
11·00	1·0508	12·25	1·0567	13·50	1·0626
11·25	1·0520	12·50	1·0579	13·75	1·0638
11·50	1·0532	12·75	1·0591	14·00	1·0651
11·75	1·0544	13·00	1·0603	14·25	1·0663
12·00	1·0555	13·25	1·0614		

M. M. P. M.

Gravimetic Estimation of Dextrose by means of an Alkaline Copper Solution. By M. Maercker (*Chem. Centr.*, 1878, 584—587).—Soxleth (this Journal, 1878, Abs., p. 686) from his experiments concludes that a gravimetic estimation of sugar by means of an alkaline copper solution is impossible. The author, while granting the accuracy of Soxleth's experimental results, denies his conclusion. If the precipitated cuprous oxide be collected on a filter heated, in hydrogen and the copper weighed, a small error is always introduced, but by means of a formula deduced from experimental data, curves may be constructed by the aid of which very accurate results are attainable.

M. M. P. M.

Estimation of Dextrose and Inverted Sugar in Presence of Saccharose. By Heinrich (*Chem. Centr.*, 1878, 409—414).—Strohmer and Klaus have shown that Sachsse's method with an alkaline solution of mercury iodide is inapplicable for the determination of dextrose in the presence of saccharose (see this Journal, 1878, Abs., p. 246).—The author finds, however, that by using a solution containing less potash than originally directed by Sachsse, dextrose may be correctly determined in the presence of very varying amounts of saccharose. The test liquid as prepared by the author contains 25 grams potassium iodide, 18 grams mercuric iodide, and 10 grams potash in 1,000 c.c. water. For the determination of small quantities of inverted sugar not more than 5 c.c. (preferably 2·5 c.c.) of the standard liquid should be employed, which should be previously titrated against a very dilute sugar solution, prepared by inverting saccharose. If less than 0·1 per cent. inverted sugar be present in the liquid under examination, 2·5 c.c. of a solution, prepared by dissolving 10 grams of potash in 1,000 c.c. water, should be added to each 2·5 c.c. of the standard solution before titration.

The author's experiments show that the standard potassic-mercuric iodide liquid containing only 10 grams potash per litre is not affected by ammonium salts.

M. M. P. M.

Quantitative Estimation of Starch in Paper. By C. Wurster (*Dingl. polyt. J.*, **229**, 538—540).—Starch is of very general occurrence in paper, and may be very readily detected by moistening the latter with a dilute solution of iodine, the intensity of the violet to blue coloration often forming the only means employed to ascertain the quantity of starch present. The quantitative estimation can be undertaken in two ways: by dissolving the resin and starch out of the paper and weighing the latter, or by converting the dissolved starch into sugar, by means of continued boiling with dilute acids or by the addition of malt extract, and determining the sugar by titration in

the usual manner. The author has used the former method in his determinations. He first estimates the quantity of water present, then the resin, by boiling out with alcohol, to which a few drops of hydrochloric acid are added, the starch is next dissolved by boiling the paper for some time with equal parts of water and alcohol, to which a few drops of hydrochloric acid are added, and weighing the residual paper. Since the hydrochloric acid causes a certain loss in mineral constituents, the ash must be determined in the raw and in the extracted paper, and the difference, which is almost constant and amounts to about 0·8 to 1·1 per cent., deducted from the resin. In this manner concordant results are easily obtained.

The following analysis were made:—

Paper.	Water.	Resin by means of alcohol.	Resin by means of ether.	Starch.	Ash.	Fibre as residue.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Fine post, thin	7·2	2·9	—	3·5	1·8	84·6
Fine post, medium strong	7·6	5·4	—	3·1	1·9	82·0
Fine post, strong.....	7·2	3·4	—	3·7	7·8	77·9
Common writing paper containing much woody matter.....	5·8	3·9	—	9·1	33·4	47·8

D. B.

Hehner's Method of Testing Butter. (*Dingl. polyt. J.*, **229**, 282—284.)—This method of testing butter, described in *Dingl. polyt. J.*, **228**, 215 and 404, depends on the estimation of insoluble fatty acids, the percentage of which, in a good butter, according to Hehner, should be 88. Some experimenters find this number too low, whilst Heintz (*ibid.*, **229**, 228—478) finds the method untrustworthy. According to Völker and Bromeis, butter consists of—

68 per cent. tris-tearin and tri-palmitins,
30 ,, tri-olein,
2 ,, other glycerides.

As this is not in accordance with Hehner's results, Fleischmann and Vieth (*Zeits. Anal. Chem.*, 1878, 287) have investigated the subject, and find that butter may contain from 88·79 to 89·73 per cent. of insoluble fatty acids. Some artificial butters were found to contain 95·57 per cent., whilst various samples of tallow yielded percentages from 95·2 to 95·8, and in olive oil 96·14 per cent. of insoluble fatty acids were found; these are very quickly oxidised.

From this it would seem that if a butter contains 90 per cent. or more of insoluble fatty acids, it is probably adulterated butter; yet with the limit 89·8 per cent. for insoluble fatty acids, it is possible for many adulterated butters to pass undetected. The cause for this appears to be more in the method of operating than in the principle of the method; but it would certainly be more accurate if some better

method were devised for separating the soluble from the insoluble fatty acids than washing with hot water. P. P. B.

Distinctive Tests for Phenol, Cresol, and Creasote. By A. H. Allen (*Analyst*, 1878, 319—324).—The following experiments were made with a view of ascertaining the most trustworthy tests for distinguishing phenol and cresol from wood-tar creasote. The phenol was a sample of Calvert's No. 1, for internal use, b. p. 182°. The cresol was prepared from Calvert's No. 5 by fractional distillation, the portion coming over between 195° to 205° being collected separately and again distilled. The cresol thus obtained boiled at about 197°. The creasote was a sample of Morson's wood-tar creasote. It boiled at 217°.

Phenol was found to take up from 26·6 to 27 per cent. of water, a fact which is of importance, as showing that it will take up far more water than is commonly supposed. The proportion is also of interest, as it corresponds closely with the formula $C_6H_6O.2H_2O$. Cresol absorbs water, amounting to 13 per cent. of the hydrated acid. $C_7H_8O.H_2O$ requires 12·7 per cent.

1. *Action of Cold.*—Dry pure phenol is solid at ordinary temperatures, and the wet substance solidifies in a freezing mixture of hydrochloric acid and sodium sulphate. Cresol and creasote show no signs of freezing on exposure to the same degree of cold.

2. *Solubility in Water.*—1 vol. of phenol dissolves in 11·1 of water. In hot water phenol is still more soluble. Cresol dissolves in about 31 parts of water.

3. *Solubility at* 15·5° *in Solution of Caustic Soda containing* 6 *per cent. of Caustic Soda.*—Dry phenol is completely soluble in an equal volume of soda solution containing 6 per cent. of pure NaHO (free from alumina). Dry cresol is insoluble in small proportions of 6 per cent. soda solution. Creasote is practically insoluble in 6 per cent. soda.

4. *Soluble at* 15·5° *in Solution of Caustic Soda containing* 9 *per cent. of Caustic Soda.*—Dry phenol is soluble in an equal measure of 9 per cent. soda. On addition of any proportion of water up to 7 vols. the liquid remains clear, but is precipitated by 8 vols. of water. Dry cresol is soluble in an equal measure of 9 per cent. soda, but is precipitated when the proportion of the reagent is increased to $3\frac{1}{2}$ vols. Creasote is insoluble in any smaller quantity than 2 vols. of 9 per cent. soda.

5. *Solubility at* 15·5° *in Solution of Ammonia* (*sp. gr.* 0·880).—Dry phenol is completely and readily soluble in an equal volume of strong ammonia. Cresol is almost insoluble in ammonia, creasote practically insoluble.

6 and 7. *Behaviour with Benzene, Chloroform, Carbon Bisulphide, or Ether.*—Dry phenol, cresol, and creasote are miscible with these liquids in all proportions.

8. *Behaviour with Petroleum Spirit of sp. gr.* 0·699.—Dry phenol dissolves half its volume of petroleum spirit, forming a clear liquid. It is permanently soluble in about ten measures of petroleum spirit at 15·5°. Phenol and hot petroleum spirit are miscible in all proportions. Hydrous phenol is almost insoluble in moderate quantities of

cold petroleum spirit, which does not separate the contained water from it. Dry cresol is miscible with petroleum spirit in all proportions. Cresol is only very sparingly soluble in petroleum spirit. Creasote is miscible with petroleum spirit in all proportions.

9. *Behaviour with Glycerin of* 1·258 *sp. gr.*—Dry phenol and cresol are miscible with glycerin in all proportions. Creasote is insoluble.

10. *Behaviour with Collodion.*—Dry phenol or cresol, when shaken with half its measure of collodium (B.P.), precipitates the nitro-cellulose in a transparent gelatinous form, very difficult to see. Creasote does not precipitate the nitro-cellulose from collodion, but mixes perfectly with its ethereal solution.

11. *Reaction with Ferric Chloride.*—The addition of one drop of a 10 per cent. aqueous solution of ferric chloride to 15 c c. of an aqueous solution of phenol or cresol, causes a permanent violet-blue coloration. When creasote is similarly tested, a blue colour is produced, which almost instantly changes to green and brownish-yellow.

From the foregoing details it will be seen that phenol, cresol, and wood-tar creasote can be readily distinguished from each other. The case, however, is very different when we have to deal with a mixture of the three substances, such as occurs in the case of a sample of creasote adulterated with crude phenol. In such a case many of the tests are greatly reduced in value or rendered absolutely worthless.

As phenol, cresol, and creasote boil at temperatures tolerably widely apart, the author thought it might be possible to effect a sufficient separation by fractional distillation to enable the test for the coal-tar acid to be more readily applied. For this purpose a mixture of No. 5 carbolic acid and Morson's creasote was introduced into a small retort, and the liquid distilled. The water, which came over first, was collected separately. The next portion of the distillate was boiled to free it from a little water, and was then tested with glycerin and with collodion. It dissolved readily in the glycerin, and precipitated half its volume of collodion. Hence the phenol of the mixed creasote was fairly detected, and there seems no reason why fractional distillation should not serve for the detection of smaller proportions of phenol, as it will certainly be most abundant in the first portion of the distillate. The ferric chloride test was not found of service for testing the distillate, sufficient creasote being present to produce a decided brown coloration. D. B.

Detection of Gypsum, Heavy Spar, &c., in Meal. By R. Böttger (*Chem. Centr.*, 1878, 638).—A very small quantity of the suspected meal is brought into the Bunsen lamp, after moistening with hydrochloric acid, and the flame is examined by means of a spectroscope. M. M. P. M.

Complete Precipitation of Albumin from Animal Fluids. By F. Hofmeister (*Chem. Centr.*, 1878, 635—639).—The greater portion of albumin is separated from the liquid by the ordinary means by boiling the slightly acid liquid. The filtrate is then boiled for a few minutes with lead hydrate, freshly precipitated lead carbonate, oxide,

or zinc oxide, and again filtered. The second filtrate is entirely free from albumin. The albumin is precipitated in the form of a metallic compound. If the liquid contains considerable quantities of phosphates or sulphates, the addition of a little lead acetate, previous to boiling with lead hydrate, is necessary, in order to prevent the formation of free alkali, which would transform small quantities of albumin into soluble alkaline albuminate.

It is further shown by the author that animal liquids which give no precipitates when treated with potassium ferrocyanide and acetic acid, or with the alkaloïd reagents, viz., tungstophosphoric acid, potassium-mercuric iodide, potassium-bismuth iodide, and tannic acid, are entirely free from albumin and peptones. If, on the other hand, a precipitate is produced by an alkaloïd reagent, but not by potassium ferrocyanide and acetic acid, the presence of peptone-like bodies is rendered exceedingly probable. M. M. P. M.

Technical Chemistry.

Intensifying Photographic Negatives by Means of Potassium Sulphide. (*Chem. Centr.*, 1878, 623.)

Preparation of Finely-divided Metallic Oxides. (*Chem. Centr.*, 1878, 605.)—By burning mixtures of metallic salts with resin, spread upon iron plates, with free access of air, oxides may be produced in a state of very fine division, fit for enamelling.

M. M. P. M.

Numeite, a New Jewel. By R. v. Wagner (*Dingl. polyt. J.*, **229**, 541).—Most of the French nickel manufacturers prepare the metal, its alloys, and salts used for nickel plating, from "garnierite," an ore found in New Caledonia, and having the following composition:—

NiO.	Fe_2O_3.	MgO.	SiO_2.	H_2O.
18	7	15	38	22 = 100

The ores are found in serpentine, and possess a fine grey colour resembling malachite. The latter circumstance, and the steatite-like consistency of the minerals, have given occasion to work up selected pieces of garnierite as brooches, earrings, &c., under the name of numeïte. Numeite is dense, and can therefore not replace the fibrous and satiny malachite as a jewel; it may, however, like lapis lazuli, find some application in mosaic work, or as ornaments. The malachite imitations, which are at present worn in Paris as earrings, necklaces, bracelets, &c., must not be confounded with the numeite jewels. These imitations consist of green-coloured, tastefully marbled celluloïd. D. B.

Use of Chrome Alum instead of Potassium Dichromate in Wool Dyeing. By V. Joclet (*Dingl. polyt. J.* **229**, 288—289).—By employing chrome alum not only is a greater regularity obtained, but the use of cream of tartar is obviated. The wool is boiled for one hour and a half in a chrome alum bath, and is thereby coloured bluish-green. The colour is stable, and bears exposure, which is not the case when potassium dichromate is used. For blues and greens, alum and sulphuric acid are added to the bath—for blacks no sulphuric acid. For brown, sulphuric acid is used if the material is not to be dyed with madder. Copper sulphate gives darker tones, whilst addition of tin salts is made in case of violet-blues and bluish-greens. 25 kilos. require the following proportions in the chrome alum bath :—

Colour.	Alum. Grams.	H_2SO_4. Grams.	$CuSO_4$. Grams.	Chrome alum. Grams.
Brown madder..	—	—	—	650
Olive madder ..	—	—	50	630
Black	—	—	—	625
Coffee-brown ..	—	40	100	600
Dark blue	500	50	50	450
Light blue	500	50	—	400
Dark green	600	60	100	500
Light green....	300	60	—	625
Violet	500	50	40	500
			salts of tin.	

P. P. B.

Separation of Carbon, Sulphur, and Phosphorus in Open Hearth, Puddling-furnace and Bessemer-converts. By I. L. Bell (*Dingl. polyt. J.*, **229**, 184—190, and 290—295).—From a series of experiments made on this subject, it appears that carbon, silicon, and perhaps sulphur are removed from iron at low temperatures, owing to their undergoing oxidation by the oxygen from the air, or from oxidising agents such as oxide of iron or silicate of iron. Phosphorus, however, cannot be so removed, although it is oxidised at low temperatures, yet at higher temperatures it is again reduced and taken up by the iron from the slag, which contains it as phosphides of iron. Cleveland iron, the amount of phosphorus in which had been reduced to ·055 per cent., and possessed a homogeneous fracture, when heated for 3 hours in contact with a slag containing phosphorus, at a temperature equal to the final temperature of a puddling-furnace, was found to contain ·365 per cent. phosphorus. This iron had a crystalline fracture. A similar change takes place during puddling, the high temperature employed at the close of the process causing the iron to take up again a portion of the phosphorus from the oxides.

The author gives an account of experiments made with iron rails manufactured from Cleveland iron, from which it appears that it is an unsuitable material. The following analyses show the composition of such rails :—

C	0·183	0·117	0·100	0·150
Si	0·168	0·123	traces	traces
S	0·111	0·037	0·124	0·050
P	0·310	0·319	0·363	traces
Mn	0·924	0·709	traces	0·302

Such iron rails, when hardened by Dodd's process, which consists in heating them in closed retorts for 60 or 75 hours to a red heat, with charcoal and soda, yielded a rail which was far more durable, but had the fault of being too brittle.

Trials were made with rails of malleable iron manufactured from Cleveland iron and puddled in Dank's furnace; the following results from analyses of eight samples show the iron to be pure, and that the Dank's process is very effective in the removal of phosphorus:

C	from	0·046	to	0·109 p. c.
Si	„	0·078	„	0·202 „
S	„	0·005	„	0·009 „
P	„	0·074	„	0·143 „

Rails from this iron had a fine crystalline fracture, but were found not to be very durable, the iron being too soft. They are much more durable when hardened, the surface being converted into steel, the percentage of carbon in the outer surface is then about twice that contained in Bessemer steel.

It appears that rails made from Bessemer steel are about three times as durable as iron rails. The author points out that great irregularities occur in the strength of iron from the same manufacture, and often in the same rail; further, the analytical results show no cause for this, as the following analyses of two parts of one and the same rail indicate:—

	Brittle part.	Strong part.
C	0·039	0·138 p. c.
Si	0·189	0·179 „
S	0·034	0·031 „
P	0·346	0·386 „

In the latter portion of this paper the author describes his experiments upon the removal of phosphorus from iron by treatment with molten oxide of iron. An account of this has appeared in this Journal, 1878, Abs., p. 352—354. P. P. B.

Steeling Copper Plates. By R. Böttger (*Chem. Centr.*, 1878, 687).—100 parts of ammonio-ferrous sulphate and 50 parts of ammonium chloride are dissolved in 500 parts of pure water, a few drops of sulphuric acid are added, the liquid is maintained at 60° to 80°, and the copper plate is immersed in this liquid, and is made the cathode of a system of two or three Bunsen's cells, the anode consisting of an iron plate equal in size to the copper. In a few minutes the copper plate becomes covered with a hard steel-like deposit of iron.

M. M. P. M.

Manganese Alloys. By E. W. L. Biermann (*Chem. Centr.*, 1878, 592).—An alloy of copper and manganese, which the author calls

"cupro manganese," and free from iron, is prepared by some method not stated. It contains 70·5 per cent. copper, 25 per cent. manganese and 0·5 per cent. carbon. This alloy is added in small pieces to molten copper or bronze covered with charcoal and a little sodium, or potassium carbonate. Many other alloys may be prepared in like manner. The absence of oxygen renders these alloys very ductile and easily worked. M. M. P. M.

Preparation of Inverted Sugar. (*Chem. Centr.*, 1878, 703).—Patent of Maumené, Cail, and Co. The principle is the same as that of the processes employed in the laboratory, the sugar being boiled with very dilute sulphuric acid. Details of manufacture may be obtained from the paper or patent. Inverted sugar is said to keep well, to be easily prepared and to be sweeter than cane sugar: it is applicable for many purposes. M. M. P. M.

Ly-chô, a New Thickening-material. By G. Vaucher (*Dingl. polyt. J.*, **229**, 289—290).—This is a description of thickening-material introduced by A. Tissot in Asnières. Ly-chô is a white, slightly yellow powder, resembling dextrin in appearance, and has an odour resembling that of tea. Digested with cold water for 24 hours, a thickening-material is obtained, which can be diluted with water. Treated with nitric acid, it yields mucic and oxalic acids, and with hydrochloric acid, glucose. On ignition it leaves 14 per cent. ash. Its aqueous solutions are precipitated by ferric salts, basic nitrate and acetate of lead, also by mercuric nitrate and alcohol. With iodine it yields a red coloration. This material may be substituted in most cases for gum tragacanth with considerable advantage. P. P. B.

Mordant for Turkey-red Dyeing. By A. Müller-Jacobs (*Dingl. polyt. J.*, **229**, 544—546).—In 1877 the authors took out a patent for the preparation of Turkey-red mordant for dyeing and printing on spun and woven stuffs with madder and all its preparations, including artificial alizarin, purpurin, and similar colouring matters. By the use of this mordant, once passing replaces the usual oft-repeated soap-baths, and yields a colour which is inferior neither in brightness nor fastness to ordinary Turkey-red. This "Turkey-red oil" is a mixture of sulpho-ricinoleate and sulpho-pyroterebate of sodium. In order to prepare sodium sulpho-ricinoleate, ordinary or purified castor-oil is treated with 20 per cent. of its weight of sulphuric acid of 66° B. After two or three hours' standing, the mass is diluted with water and neutralised with sodium carbonate. The next day the soda salt separates from the mother-liquor. The sulpho-ricinoleic acid according to the author is $C_{18}H_{34}S_4O_6 = C_{18}H_{32}O.OH.HSO_4$. For the preparation of the pyroterebate of sodium, 100 parts of colophony are boiled with 250 parts of nitric acid, and after 1 to 1½ hours' boiling the mass is evaporated slowly, and the residue heated at 200° to 250° in closed iron vessels for half an hour. When cold the semi-fluid mass is treated with 20—30 per cent. sulphuric acid at 66° B., and after two to three hours neutralised with sodium carbonate, when sulpho-pyroterebate of sodium is obtained.

To prepare the Turkey-red mordant, equal parts of the two salts are mixed together, the mixture being at once used for the preparation of Turkey-reds. Trials with chemically pure sulpho-ricinoleate and sulpho-pyroterebate of sodium gave as the most suitable proportions 6 to 7 parts of the former to 3 or 4 parts of the latter. Instead of a mixture of sulpho-pyroterebate with sulpho-ricinoleate of sodium, a mixture of sulpho-ricinoleate of sodium or ammonium with a mixture of sulpho-oleate and sulpho-margarate of sodium or ammonium can be used, which is obtained by treating olive oil with sulphuric acid, and neutralising the sulphonic acids formed with soda or ammonia. D. B.

Reduction of Indigo by Glycerin. By Prud'homme (*Dingl. polyt. J.*, **229**, 546).—By suspending finely powdered indigo in water containing an alkaline carbonate and adding stannous oxide and boiling, the reduction of the indigo is always incomplete. On replacing the water by glycerin, however, the reduction begins in the cold, the liquid assuming a greenish colour, and at 110° to 120° a yellow solution of perfectly reduced indigo is obtained. If the heating be continued too long, however, the indigo is not merely reduced, but also partly destroyed. This reducing action may be thus expressed: $C_3H_8O_3 + 2NaHO_2 = C_2H_3O_2Na + CHO_2Na + H_4$. From this it will be seen that the use of stannous oxide is not by any means necessary, and it has been shown experimentally that it may be dispensed with. The author has endeavoured to apply this property of glycerin to obtain a better formula for Zürcher's steam indigo-blue, but satisfactory results were obtained only when operating on a small scale. The following formula for steam-blue is given: Dissolve in 0·5 litre white glycerin, 250 grams gum Senegal, and 300 grams crystallised sodium carbonate, and add to the cold solution 45 grams of ground indigo and 150 grams of stannous oxide. The reducing action of glycerin is interesting, however. Its presence facilitates the reduction of indigo by means of zinc-dust or glucose, and the author has also found that alizarin, nitro-alizarin, and rufigallic acid are reduced when warmed with glycerin, stannous oxide and alkaline carbonate, the three colouring matters yielding a dirty-yellow liquid, which contains products in solution essentially different from the original substances. D. B.

Behaviour of Vulcanised Caoutchouc with Illuminating Gas. By G. Vulpius (*Arch. Pharm.* [3], **13**, 232).—The smell of gas having been observed in the neighbourhood of a vulcanised caoutchouc tube through which gas was passing, it was thought that the gas was absorbed by the caoutchouc and then passed out by diffusion; but on exposing portions of the tube to gas in a eudiometer, no change of volume was observed, from which it would seem that the walls of the tube were more or less porous. All odour of gas disappeared when the tube was coated with soluble glass. E. W. P.

General and Physical Chemistry.

Difference of the Absorption-spectra for one and the same Substance. By H. W. Vogel (*Deut. Chem. Ges. Ber.*, **11**, 913—920, 1363—1371).—The author has already shown that one and the same body under different circumstances is capable of exhibiting absorption-spectra of totally different character, and he now finds that this property is common to almost all absorbent solid and dissolved bodies, both organic and inorganic; those bodies which give in the solid state the same spectrum as in the dissolved, belong to the exceptions. Hitherto it has been almost universally believed that the spectrum of a salt or colouring matter in solution is identical with that of the solid body. The author's investigations show that this assumption is no longer tenable.

Potassium Permanganate.—In sufficiently dilute solution, an absorption-spectrum is obtained with five very distinct bands between D and F, and two less distinct beyond F. The evaporated solution furnished a bluish efflorescence, in thick layers of a beautiful red. This gave the same bands as the solution, and in just the same position. But if the spectrum of the solid body be compared with that of an equally strongly coloured solution, then it is observed that the character of the spectrum of the solid body is very different from that of the dissolved.

Uranium Nitrate, $UO_2(NO_3)_2 + 6H_2O$.—Morton and Bolton have already investigated the spectra of this body in the solid state and in solution, and have described the striking spectral differences of different closely allied uranium compounds. They observed numerous absorption-bands in the blue and violet, which in diffused daylight are only partially visible.

The reactions of the salt dissolved in water and in alcohol are similar, but still quite distinguishable from one another by differences in position and character of the bands. The band on F has the same position in both solutions, but both the other bands are, on the contrary, considerably advanced towards the violet in the alcoholic solution. The contrary would have been expected in the more refractive solution according to Kundt's rule.

A characteristic difference is observed between the absorption-spectra of solid and liquid bodies, and those of the glowing vapours of the elements. With the latter, the absorption-lines have a fixed position, characteristic for each body. The position is thus characteristic for the glowing substance. With the absorption-spectra of cold bodies, liquid or solid, the absorption-bands of different bodies often show exactly the same position, so that position is not characteristic. A positive difference between solid, liquid, and gaseous bodies seems to be, that the absorption-bands of the latter may be resolved into lines by sufficient dispersion, but those of the former cannot.

Cobalt Compounds.—Interesting through the multiplicity of their

spectral phenomena. Of their spectra, that of cobalt glass is best known. In a thick layer, only blue passes through; in thinner, a shadow appears in the green and an absorption of the red and yellow; in yet thinner layers, three bands are recognised. These three bands have been observed in fresh cobalt hydrate, precipitated by potash from dilute solution and suspended in the liquid. The coincidence of the spectra of two bodies like cobalt glass and cobalt hydrate, which besides the cobalt and oxygen, have nothing in common either in their physical or in their chemical properties, is very remarkable. A still more remarkable difference is observed with cobaltous chloride, $CoCl_2$ in different states of hydration.

The solutions of cobaltous chloride in absolute alcohol, in concentrated and dilute conditions give again modified spectra, yet still with points of resemblance to the cobalt glass spectrum. If the spectrum of this alcoholic solution be compared with that of the deep blue cobaltous chloride, then an analogy of certain bands is perceived, but these, in opposition to Kundt's law, are advanced in the aqueous solution more towards the red than in the alcoholic solution. Cobalt, in short, in the equally saturated conditions its different compounds, shows one of the most remarkable examples of a "changeability of spectrum."

Chromic Compounds.—Of the chromic compounds, the spectrum of the violet chrome-alum in aqueous solution is best known. The violet chromic chloride in solution absorbs similarly but more powerfully than chrome-alum. The absorption of the green chromic salts in aqueous solution is not very different from that of the violet. Solid chrome-alum behaves quite differently. The blue is absorbed in the same manner as as in the solution, but the spectrum of the solid green chrome-alum departs very considerably from that of the solid violet salt. Whilst chromic chloride dissolved in water shows the same spectrum as solution of chrome-alum, the solution of the chromic chloride in alcohol behaves differently. Borax glass coloured with chromic oxide absorbs very similarly to chromic chloride in alcohol.

Cupric sulphate is one of the few substances showing the same absorption-spectrum in the solid state and in solution. It extinguishes the red up to wave-lengths of 620, then the absorption diminishes quickly and terminates in the yellowish-green. Green, bright blue, and dark blue pass through unweakened, but the violet is again partially absorbed. Special bands do not show themselves.

Iodine is one of the few bodies which allow an investigation of their absorption-spectra in the solid, dissolved, and gaseous form. The spectrum of the violet vapour already observed by Brewster, exhibits with a certain thickness a great number of fine lines, from red to violet, and with greater thickness growing to intense bands. The appearance of iodine in solution is quite different. The bisulphide of carbon solution is violet, a homogeneous shadow being observed in concentrated solutions between C and D, in dilute between D and F, but without a trace even of lines or bands. In the yellow alcoholic solution there is only an absorption of the blue side of the spectrum, stretching more or less towards the red according to the concentration. Solid iodine in plates shows only a grey colour and a partial

extinction of all rays of the spectrum. The beautiful spectrum of iodine vapour is not recognised again either in the solid or liquid conditions.

Nitrogen Tetroxide, as a gas, exhibits the known and well-marked spectrum with lines. Kundt describes the spectrum of the liquid body as composed of dull black bands, agreeing as to position with the absorption-bands of the vapour. Gernez confirms this, and asserts that the benzene and carbon bisulphide solutions behave similarly. The author, speaking of the benzene solution, says the position of the bands agreed with that of certain groups of lines in the vapour spectrum, but differed considerably in character; they formed broad bands in which no lines were seen, or only faint indications. The solution, in spite of its intense colour, exhibited a much weaker absorption of the green and yellow, than only a thin, faint-coloured layer of the gas would do. Only in the red were lines perceptible. The molecular vibrations which proceed in the gas freely, and form waves of definite length, appear confused in the solution and destroyed by intermediate tones. According to Kundt, a displacement in the strongly refractive solution of the bands towards the red should be expected, but this does not take place.

As the result of his investigations with solid and liquid (dissolved) organic colouring matters, the author arrives at the following conclusions:—

I. Between the spectra which a body gives in the solid, liquid (in solution), and gaseous conditions, there exist very considerable differences. Characteristic bands which make their appearance with a substance in the solid state, do not reappear in the others, or in very altered positions, or else with altered intensity or appearance. Cupric sulphate and chlorophyll exhibit the same absorption in the solid as in the dissolved state. *Examples of those showing bands in solid state, which are not to be found in the states of solution or gas:* Chrome alum, cobaltic chloride, iodine, bromine, fuchsine, naphthalene-red, indigo, cyanine, aniline-blue, methyl-violet, eosin, carmine, purpurin, alizarin, santonin. *Examples of those whose bands present an altered appearance:* Uranic nitrate, potassium permanganate, nitrous acid, alkanna-red.

II. The spectra which one and the same body gives in different solvents, are not to be distinguished in many cases. (*Examples.* Purpurin in alcohol and in carbon bisulphide, methyl-violet and indigo-sulphonic acid in water and in amyl alcohol). In other cases only by the position of the bands. (*Examples.* Blue cobalt chloride, fuchsine, corallin, eosin in water and in alcohol.) In other cases, however, by the total difference of their character, so that the spectra show no kind of agreement. (*Examples.* Iodine in carbon bisulphide and in alcohol, naphthalene-red, aniline-blue, purpurin, hæmatoxylin, brasilin in water and in alcohol.)

III. Kundt's rule that the absorption-bands of a dissolved body incline further towards the red, the stronger the dispersion of the fluid is for the region of the absorption-band, does not hold in many cases. Often the absorption-bands incline towards the blue in a more refractive solution. (*Examples.* Uranic nitrate in water and in alcohol, blue cobalt chloride in water and in alcohol.) In some cases they

show an unaltered position in different media. (*Examples.* Nitrous acid in air and in benzene; indigo-sulphonic acid and methyl violet in water, in alcohol, and in amyl-alcohol; purpurin in carbon bisulphide and in alcohol.) In some cases a very strong inclination is observed according to Kundt's rule, in others a very weak inclination for the same part of the spectrum, according to the nature of the colouring matter. (*Examples.* Corallin and fuchsine.) Many bands show in the different media the same position, or nearly so, whilst others are at the same time invisible or displaced. (*Examples.* Uranic nitrate in alcohol and in water, cobalt oxide in glass and in water, uranous nitrate in neutral and in oxalic acid solution.) The author in a foot-note adds that Kundt has recently found that solvents, which with regard to refrangibility are near together, do not always obey his law. He thus modifies his paragraph on this head: "If one colourless medium has a considerably greater refractive and dispersive power than another, the absorption-bands of the substance dissolved in the medium of the greater refractive power will lie nearer to the red end of the spectrum than would be the case had the medium of lesser refractive power been employed."

IV. The position of the absorption-bands in the spectra of solid and dissolved bodies can only be taken exceptionally as characteristic of the bodies in question.

Totally different bodies show absorption-bands in exactly the same position. (*Examples.* Solid uranic nitrate, and potassium permanganate in the blue, naphthalene-red and corallin in the yellow, indigo, aniline-blue and cyanin in the orange, aldehyde-green and malachite-green in the orange.) Closely related bodies show under like circumstances striking differences in the position of their bands (solid uranium salts according to Morton and Bolton).

V. The statement that for absorption-spectra, "Each body has its own spectrum," is only admissible with great limitations (see Moser, *Pogg. Ann.*, **160**, 177). The great number of polychroic bodies show different colours and different spectra in the solid state, according as they are viewed in different directions. Bahr and Bunsen show that crystals of didymium nitrate exhibit different spectra in differently polarised light. This is to be traced to a dichroism of the didymium salts, which would have been difficult to detect without spectrum analysis by observation of colour alone. Most of the remaining bodies exhibit different spectra in the solid state from what they do in solution, and in the latter case again differ according to the solvents, so that it is a question which of these spectra is to be regarded as the proper spectrum of the substance. The most important difference of the spectra of simple bodies in the state of incandescent vapour, the position of the spectral lines, ceases to be characteristic for the absorption-spectra of liquid and solid bodies. But it is not to be expected that the spectra of liquid and solid bodies should show the characteristic differences shown by the spectra of glowing vapours. It is known that metals, which in the form of glowing vapours show such strikingly different spectra, show qualitatively the same spectrum, namely, a continuous one, as glowing liquids or glowing solids; accordingly, the absorption-spectra of these bodies can show no special characteristic

differences, if quantitative differences with regard to the absorbed colours be in question. Thus the laws with regard to the spectra of the gases of simple bodies are not applicable to the spectra of solid and liquid bodies, and in like manner researches show that with compound bodies also simple relations do not exist between the spectra which they exhibit in their different aggregate conditions.

The spectrum of a body will show itself most clearly and purely when the body is gaseous. In this condition the molecular vibrations are not hindered by cohesion, as in fluid bodies, and in a higher degree in solid ones. According to this view, the least characteristic spectra are to be expected with solid bodies, and this is attested by the majority of bodies investigated. There are bodies, however, which in the solid state show a richer and more characteristic spectrum than in the state of solution; to these belong the uranium salts, each of which shows its own peculiar spectrum in the solid state, and many concordant spectra when dissolved (Morton). The didymium salts may be also mentioned (Bahr and Bunsen). Taking these facts into consideration, it is seen that *absorption-spectrum analysis cannot base itself alone upon the recognition of the position of the absorption-bands of a body, but much rather on the alterations or changes of position of the spectra of the same body under the influence of different solvents and reagents.* For example, cyanine and aniline-blue give a very similar spectrum in alcohol, a totally different one when dissolved in water. The oxyhæmoglobin bands disappear with reducing agents, but the carmine bands do not. The band of brasilin disappears with acetic acid, that of fuchsine does not. The known characteristic alizarin-bands appear only in alcoholic solution on treatment with potash. The position of the bands becomes more characteristic in the recognition of a body if it shows several absorption-bands. Still it would be going much too far to conclude as to a coinciding, or chemical similarity of two different substances from the accidental agreements of the position of the bands: as, for example, in the cases of two such bodies as blood and chlorophyll.

Only when these bands show equal relations of intensity, and analogous changes of position under the influence of the same reagents, can a conclusion be drawn as to agreement or similarity in a chemical sense.

In a final note, the author says that the recently published researches of von Lepel on the alterations of the spectra of some colouring matters in different solvents, do not in any way alter his conclusions, but merely confirm them and furnish new and interesting evidence in their favour. W. S.

Transference of Ions. By M. Kirmis (*Ann. Phys. Chem.* [2], **4**, 503—508).—The author has determined quantitatively the transference of the ions, using for this purpose Wiedemann's (*Pogg. Ann.*, **99**) modified form of Faraday's apparatus (Experimental Researches, § 524), the india-rubber portions being, however, entirely replaced by glass. He finds that the quantity of copper transferred from the solution of its sulphate increases as the concentration of the solution diminishes.

Attempts to determine the influence of temperature were unsuccessful. T. C.

Unipolar Electrolytic Conduction. By F. Braun (*Ann. Phys. Chem.* [2], **4**, 476—484).—This is a continuation of the author's previous paper on the "Deviations from Ohm's Law in Metallic Conductors" (*Wied. Ann.*, **1**, 95). In the present experiments, psilomelan has been used; this is a compound of a base (MnO, together with Ba_2O, or K_2O) with manganese superoxide and water.

The presence of air is without influence on the phenomenon, and the resistance, which varies with the strength of the current, does not depend on the electrolytic conditions.

Graphic representations of the resistance as a function of the strength of the current show that it tends to attain a constant value both for the increasing and decreasing strength of the current, but between both of these it changes rapidly. When the current of a small induction apparatus is passed through psilomelan, the opening current passes more easily than the closing-current.

If the opening current of an induction apparatus passes more easily in one given direction, then the constant current passes most easily in the opposite direction. If this last fact be generally confirmed, it will present a remarkable analogy to other phenomena. Thus, in gases, the resistance in the discharge of the constant current is greater at the positive than at the negative pole, whilst the reverse occurs with the opening current of the induction apparatus. T. C.

The Quantity of Electricity necessary for the Complete Charge of a Platinum-Water-Cell, and the Distance between the Molecules of Liquid Water. By H. Herwig (*Ann. Phys. Chem.* [2], **4**, 465—476).—The author finds that the quantity of electricity required for the complete charging of a platinum-water-cell to the potential difference of 1 volt is equal to 0·000186 Farad, when the plates have a surface of 1 sq. cm. This value is independent of the distance between the plates and of the external resistance.

In order to derive from the above the charging value for a potential difference of 1·7 volts, it is necessary to multiply by (1·7 × 1·25), which gives 0·000395 Farad.

By means of this value and the application of his theory of rotary electrolytic molecules (*Wied. Ann.*, **2**, 566; **4**, 187), the author has determined directly the distance between the molecules of water, and finds it to be at most $\frac{186}{1,000,000,000}$ mm.

Lorenz (*Pogg. Ann.*, **140**, 644) found by a similar, although less direct method, the superior limit $\frac{100}{1,000,000,000}$ mm., and W. Thomson (*Nature*, 1870) by an entirely different method, the inferior limit, $\frac{50}{1,000,000,000}$ mm. T. C.

Monohydrated Sodium Sulphate and Dihydrated Sodium Carbonate. By J. Thomsen (*Deut. Chem. Ges. Ber.*, **11**, 2042—2045).—The salt which is separated on heating a solution of sodium sulphate, $Na_2SO_4.10H_2O$, saturated at 30°, the author finds to contain

1 mol. H_2O. This it loses on being gently heated, and is converted into the anhydrous sulphate. The formation of this monohydrated salt accords with the results of his investigation of the thermal conditions of the hydration of sodium sulphate (*J. pr. Chem.* [2], **18**, 1), with the observation that combination with the first mol. H_2O is attended by the evolution of 2360 heat-units, whereas the equivalent for each of the succeeding nine molecules is 1873 heat-units. The salt which is separated on heating decahydrated sodium carbonate, is the dihydrated carbonate. This salt readily parts with 1 mol. H_2O in dry air. The thermal equivalents of hydration are, for the first mol. H_2O, 3382 heat-units, for the second, 2234 heat-units, for the third and fourth, each, 2109 heat-units). C. F. C.

The "Temperature-surface" of Carbonic Acid. By A. Ritter (*Ann. Phys. Chem.* [2], **4**, 550—554).—The following equation, which has a form similar to that for superheated steam (*Ann. Phys. Chem.* [2], **3**, 447), represents, in the case of gaseous and superheated carbonic acid vapour, the relation between the pressure, specific volume, and absolute temperature: $T = 533\ pv + \frac{3}{pv\sqrt{v}}$.

$T(= 273 + t)$ indicates the absolute temperature, v the volume in c.c. of a kilogram of carbonic acid, and p the pressure in atmospheres. This equation holds good (at least approximately) for the lower and also for the higher portions of the "temperature-surface," whilst for the lower portions of this surface bordering on the "mist-margin," Andrews's observations may be used for correction.

The paper is accompanied by a table and diagram representing the above relations. T. C.

Density and Decomposition of Nitric Oxide. By A. Naumann (*Deut. Chem. Ges. Ber.*, **11**, 2045—2048).—The results of this investigation, which was completed in 1871, are published with reference to a recent paper by L. Troost (*Compt. rend.*, **86**, 1395). The author establishes, by a series of twenty observations at temperatures varying from −6° to 225°, that, the temperature remaining constant, the percentage resolution of N_2O_4 into NO_2 (calculated from the observed density by the formula $p = \frac{100(d - D)}{D}$) is increased by decrease of pressure. The relations subsisting between these three factors are elucidated by the results of observations made with each severally constant, the two others varying:—

Temperature Constant.

Temperature.	Pressure.	Density.	Decomposition.
18·0°	279 mm.	2·71	17·3 p. c.
18·5	136	2·45	29·8
20·0	301	2·70	17·8
20·8	153·5	2·46	29·3

Pressure Constant.

Temperature.	Pressure.	Density.	Decomposition.
10·5°	163 mm.	2·73	16·5 p. c.
21·5	161	2·38	33·7
14·5	175	2·63	20·9
16·8	172	2·55	24·7
17·5	172	2·52	26·2
1·0	138	2·84	11·9
18·5	136	2·45	28·8
22·5	136·5	2·35	35·3

The quotient of the percentage decomposition by the difference of temperature, in the above observations, increases with increase of temperature, in accordance with the general law of dissociation (Naumann, *Annalen*, 1868, Suppl., **6**, 205) :—

Decomposition Constant.

Temperature.	Pressure.	Density.	Decomposition.
26·7°	755·5 mm.	—	19·96 p. c.
16·0	228·5	—	20·00
35·4	755·5	—	25·65
16·8	172·0	—	26·20
39·8	755·5	—	29·23
20·8	153·5	—	29·30

The results given in the above are those of Deville and Troost. The quotient of difference of pressure by difference of temperature decreases, *i.e.*, change of pressure becomes relatively more effective than change of temperature, as the decomposition increases to 50 per cent.

The relation of decomposition to pressure, clear as it is, appears to be no more capable of simple mathematical expression than that of boiling point to pressure. C. F. C.

Dissociation of Ammonium Chloride: a Lecture Experiment. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 2004).—The dissociation of ammonium chloride may be shown by heating the substance in a bulb-tube made of hard glass which is held in a nearly horizontal position: the ammonia which escapes at the upper end of the tube will turn a piece of litmus-paper blue, whilst the hydrochloric acid which escapes from the lower end will redden litmus-paper.

W. C. W.

Modified Vapour-density Determination. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, **xi**, 1684—1685).—Instead of the simple **U**-tube, one is now employed which on one end carries an additional piece with bulb, whilst on the open limb, a little above the bend, another bulb is blown. The open end is loosely fitted with a cork, carrying a funnel-tube drawn to a point. The mercury contained in the open limb is poured out so that the level stands between bend and bulb on that limb, and thus the substance may easily be introduced.

The heating is conducted in a transparent vessel through which the vapour of a high-boiling liquid is passed. On volatilisation of the substance, the difference of levels is at once observed in both limbs. The point of the funnel-tube is now also brought down exactly to touch the mercurial surface, and after the cooling, mercury is allowed to flow in from a burette until the mercurial surface is again raised to meet the point of the funnel-tube. The volume of mercury required is easily calculated into that of the vapour.

Vapour-density at a Higher Temperature in a Vacuum.—A glass tube is drawn out at one end to a point and sealed; the other end is narrowed; and after introducing the weighed substance, the tube is exhausted of air by the water air-pump. The tube sealed up at this end also is placed in a horizontal iron tube enclosed in another, which is filled with the vapour of boiling mercury or sulphur. 15—20 minutes suffice to convert the substance into gas. The projecting end of the tube is broken, when air rushes in to fill the space not already occupied by the vapour and is then sealed up again. On cooling, the point is again broken under mercury, which rushes in and fills the space occupied by the vapour, leaving a volume, equal to that of the air which has rushed in. The difference between the total tube-volume and the air-volume gives the vapour-volume. W. S.

Determination of Specific Gravities. By W. A. Tilden (*Chem. News*, **38**, 300).—The author recommends that in publishing results, chemists should in all cases mention the experimental data from which the specific gravity is to be calculated, or at least the method of calculation. A great deal of trouble in the way of re-calculation would be saved if some uniform procedure were generally adopted. At the present time the very common practice in determining the specific gravity of a liquid is to weigh the liquid and the water successively in the same vessel at the same temperature. This plan recommends itself on the score of simplicity; but it has one disadvantage, viz., that if the specific gravity has been determined at two or more temperatures, the numbers so obtained are not available without correction for the calculation of the coefficient of expansion of the liquid.

The author prefers to proceed thus:—Fill the specific gravity bottle or tube with water, carefully adjusting the temperature to 4°; weigh with proper precautions, and record the result once for all. This gives not only the weight of the water at 4°, but the capacity of the vessel in cubic centimetres. From this the capacity at any other temperature can be calculated by the well-known formula $V = v(1 + kt)$. The coefficient of expansion of glass, k, may be taken as 0·000026; t is the difference of temperature from 4°. A table of values can thus be drawn up and kept with the specific gravity bottle.

In conclusion the author mentions, that, except for rough purposes, he has discarded all specific gravity bottles as being completely unmanageable. The use of Sprengel's tube described in this Journal, [2], **11**, 577, has given much better results. D. B.

Law of Molecular Volumes. By H. Schröder (*Deut. Chem. Ges. Ber.*, **11**, 2017—2026).—The molecular volumes of a large number of

lead and potassium salts have been determined by the author, who finds that in certain groups of compounds the predominating stere of an element is subject to minute modifications, *e.g.*, the potassium stere is 6·00 in the carbonate nitrate and selenate, but in the sulphate and chromate it is only 5·95. Each atom of the "organic elements," carbon, hydrogen, oxygen, and nitrogen, generally occupies one stere.

W. C. W.

Law of Molecular Volumes. By H. Schröder (*Deut. Chem. Ges. Ber.*, **11**, 2128—2136).—*Barium and Strontium Stere.*—An accurate determination of the molecular volumes of 29 compounds of these metals, viz., (α.) Carbonates, sulphates, selenates, and chromates. (β.) Succinates and salts of the fatty acids, formic, acetic, &c. (γ.) Various salts, such as nitrates, chlorides, and chlorates; and (δ.) Methyl sulphates, ethyl sulphates, &c., proving them to be simple multiples of $\overline{5·8}$ to $\overline{5·85}$, establishes beyond doubt the barium and strontium stere.

(α.) The volumes of their sulphates have been determined with great accuracy:—

Heavy spar ($BaSO_4$)	=	52·2
Celestine ($SrSO_4$)	=	46·4
Difference Ba − Sr	=	5·8

Since, moreover, these volumes are divisible by their difference, without remainder, it is evident that the steres of both metals and of their sulphates are equal. $BaCO_3$ (precipitated) has the same volume as $SrSO_4$, and differs, therefore, by one stere from that of $BaSO_4$.

The following are the volume-molecules for salts of the class (α):—

		As observed.
Barium carbonate, $\overline{Ba^4_1C^1_1O^3_3}$	$= 8 \times \overline{5·85}$	$= 46·80$
Strontium carbonate, $\overline{Sr^3_1C^1_1O^3_3}$..	$= 7 \times \overline{5·85}$	$= \overline{40·95}$
Barium sulphate, $\overline{Ba^4_1S^2_1O^3_4}$	$= 9 \times \overline{5·80}$	$= \overline{52·20}$
Strontium sulphate, $Sr^3_1S^2_1O^3_4$	$= 8 \times \overline{5·80}$	$= 46·40$
Barium chromate, $Ba^4_1Cr^3_1O^3_4$	$= 10 \times \overline{5·85}$	$= 58·50$

For the metal strontium the author has observed $Sr^6_1 = 6 \times \overline{5·85}$; in the above salts it is present, therefore, as one-half the volume-atom.

(β.) On comparing the volumes of barium succinate and carbonate:—

Barium succinate	$= BaC_4H_4O_4$	$= 93·7$ (observed).
Barium carbonate	$= BaCO_3$..	$= 46·8$ „
Difference ..	$= C_3H_4O$..	$= 46·9 = 8 \times \overline{5·86}$

It is seen that a difference in composition of C_3H_4O, *i.e.*, 8 elementary atoms, determines a corresponding volume-difference of 8 Ba-steres.

The volume-molecule of the succinate is—

$$Ba^4_1C^4_4H^4_4O^4_4 = 16 \times \overline{5·85} = 93·6, \text{ as observed.}$$

Similarly a difference of CH_2O between the formate and carbonate determines a volume-difference of 4 Ba-steres. The barium salts of the fatty acids exhibit a volume-difference of 3 steres for each increment of CH_2, as has been previously observed for silver and potassium salts. The propionate, however, constitutes an exception, the observed volume (143·7) differing from the calculated (140·4).

In strontium formate, the water of crystallisation occupies the normal volume; thus—

$$\text{Strontium formate} = \overline{Sr^3_1}C^2_2H^2_2O^4_4.(H^1_4O^2_2) = 16 \times \overline{5{\cdot}85} = \underline{93{\cdot}60}$$

(γ.) The halogen salts of barium and strontium also contain the steres of the metals ($BaCl_2$ excepted, for which the Cl-stere, $\overline{5{\cdot}4}$, was observed).

The constituent elements of barium hypophosphite retain their normal volume constitution, thus:—

$$\text{Barium hypophosphite} = Ba^4_1H^1_4P^1_2O^4_4 = 16 \times 5{\cdot}85 = 93{\cdot}6, \text{ as observed.}$$

The investigation of the barium salts of the halogen oxy-acids confirms the previous observation that chloric, bromic, and iodic acids are isosterides.

In the nitrates of barium and strontium the condensation of the metals is different, viz., $\overline{Ba^6_1}$ and Sr^4_1; the nitrous molecule being $N^1_1O^3_3$.

(δ.) Of the series of alcohol sulphuric acids, the volumes of the Ba-salts of ethyl-, isobutyl-, and amyl-sulphuric acids alone are divisible by the Ba-stere, without remainder. The normal volume-difference, $CH_2 = 3$ Ba-steres, obtains for these three salts. The metal is present in these salts as $\overline{Ba^6_1}$, and occupies, therefore, the same volume as potassium in the corresponding salts. The volume constitution of the sulphion is unaltered. C. F. C.

Gelatinous Silica. An Inorganic Membrane. By F. Ullik (*Deut. Chem. Ges. Ber.*, **11**, 2124—2128).—The author has succeeded in attaching gelatinous silicic acid, precipitated by hydrochloric acid from a dilute solution of sodium silicate, to glass, and by subsequent washing rendering it fit to act as a dialysing membrane. This was prepared in two forms: (1) as a free membrane 3 mm. in thickness, and (2) as a thin film (0·5 mm.), deposited upon a base of Swedish filter paper. The following are some of the author's results obtained with these dialysing agents:—

(1.) *Thick Free Membrane.*—(*a*) 50 c.c. of a solution of cane sugar (20 per cent). In three days 14 per cent. of the sugar had dialysed, the water in the dialyser standing 12 mm. higher than that outside, originally at the same level. (*b*) 50 c.c. sodium chloride solution (20 per cent.). In three days 51 per cent. of the NaCl dialysed; difference of level 15 mm. (*c*) 20 c.c. dextrin solution (10 per cent.). In three days 4 per cent. dialysed; difference of level 3 mm.

(2.) *Thin Attached Membrane.*—(*a*) 50 c.c. sugar solution (20 per cent.). In three days 49·5 per cent. dialysed; difference of level

20 mm. (*b*) 50 c.c. sodium chloride (20 per cent). In 36 hours 64·2 per cent. dialysed; difference of level 8 mm.

By way of lecture experiment a glass funnel, to the wide mouth of which a membrane of silicic acid had been attached, was inverted, and depressed to the apex in water, the interior containing a concentrated solution of copper sulphate, and the liquids without and within being adjusted to the same level. In 24 hours a rise of 13 mm. in the funnel tube was observed. C. F. C.

Inorganic Chemistry.

Preparation of Nitrous Acid. By G. Lunge (*Deut. Chem. Ges. Ber.*, **11**, 1641—1644).—Continuation of a former communication (*Ber.*, **11**, 1229). In the present one it is found that in order to prepare nitrous acid almost entirely free from nitrogen tetroxide, a nitric acid must be used of 1·30 to 1·35 specific gravity at 25° ("volumgewicht"), and that, whether starch or arsenic tri-oxide be employed as reducing agent. Stronger nitric acid than this gives the more nitrogen tetroxide the stronger it is, and this is most marked with arsenic tri-oxide. It is perhaps owing to a secondary action of the nitrous acid formed on the nitric acid. W. S.

Ammonium Nitrate. By S. Pickering (*Chem. News*, **38**, 267).—Although the melting point of ammonium nitrate is given in various text-books at 107·8—108° C., the author states that the crystallised substance dried at 100° invariably melted at 165—166°, whether recrystallised from water or alcohol. Ammonium nitrate dissolves easily in alcohol, but is much less soluble in this liquid than in water. On cooling or on evaporation, it is deposited either from its alcoholic or from its aqueous solution in anhydrous crystals, which deliquesce only when exposed to very moist air. Ammonium nitrate is insoluble in ether. On being heated above its melting point, it begins to decompose into nitrous oxide and water at about 185°, and not at 250°, as stated in Miller and elsewhere. D. B.

Sulphuric Hydrochloride and Dichloride. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, **11**, 2058—2061).—A close approximation to the theoretic yield of sulphuric hydrochloride is attained by saturating the crystallised fuming sulphuric acid of commerce with dry hydrochloric acid gas, distilling, and rectifying the product. It boils, according to the authors' observation, at 150·7—152·7°. The reversal of the above decomposition, which is usually asserted to occur, appears to be prevented by the excess of the mass of hydrochloric acid present.

In converting this chloride, $SO_2.OH.Cl$, into sulphuric dichloride, SO_2Cl_2, by Behrend's method (*Ber.*, **8**, 1004), *i.e.*, by heating it in sealed tubes at 170—180°, they have always observed the formation of

chlorine and sulphurous anhydride. From the previously established fact that sulphuric dichloride is not dissociated into these gases under conditions similar to the above, even when the temperature is raised to 230—250°, it may be concluded that they are direct products of the reaction. The decomposition therefore probably occurs in two stages, according to the equations:—

$$2SO_2(OH)Cl = Cl_2 + OH.SO_2.SO_2.OH.$$
$$OH.SO_2.SO_2OH = SO_2 + SO_2(OH)_2.$$

By this method only a small yield appears to be obtained; thus, in one experiment 60 grams sulphuric hydrochloride, heated at 180—190° for 18 hours, yielded 17 grams of the chloride (b. p. 70°), 12 grams of sulphuric acid, and 25 grams of unaltered sulphuric hydrochloride, the remaining 6 grams being lost as SO_2 and Cl. C. F. C.

Action of Sulphuric Hydrochloride on the Chlorides of Titanium, Antimony, Tin, and Silicon. By F. Clausnizer (*Deut. Chem. Ges. Ber.*, **11**, 2011—2012).—On the addition of sulphuric monochloride to titanium chloride a yellow amorphous deliquescent powder separates out, having the composition $ClSO_2.OTiCl_3$.

Sulphuric monochloride has no action on the chlorides of antimony, tin, or silicon. W. C. W.

Sulphoselenium Oxytetrachloride. By F. Clausnizer (*Deut. Chem. Ges. Ber.*, **11**, 2007—2009, and 2009—2011).—On cooling a warm solution of selenium chloride in sulphuric monochloride, *sulphoselenium oxytetrachloride* is deposited in groups of needle-shaped crystals, which melt at 165°, and boil at 183°. This substance, which is very deliquescent, resembles the corresponding sulphur-compound, but it is not decomposed by strong sulphuric acid. The sulphoselenium oxytetrachloride can also be prepared by dissolving selenium tetrachloride in Nordhausen sulphuric acid, $H_2S_2O_7 + SeCl_4 = SO_3SeCl_4 + H_2SO_4$; or by heating in sealed tubes at 170—180° a mixture of sulphuric dichloride and selenium oxychloride, $SO_2Cl_2 + SeOCl_2 = SO_3.SeCl_4$. It is also formed by the action of sulphuric monochloride on selenium oxychloride, or on selenium di-oxide. W. C. W.

Studies of the Phosphates. By E. Erlenmeyer (*Liebig's Annalen*, **194**, 176—207).—*Dihydric ferrous phosphate*, $Fe(H_2PO_4)_2.2H_2O$ (or $Fe_2(H_2PO_4)_4.4H_2O$.—This salt is prepared by dissolving metallic iron in large excess of phosphoric acid, in a current of pure hydrogen, and evaporation in the vessel in which it is dissolved. The excess of phosphoric acid is removed by washing with ether, and the ether is evaporated in a current of hydrogen. It forms a white crystalline powder, which oxidises very rapidly on exposure to air, even when dry, turning first greyish-blue, and finally red. In nine days it was almost completely oxidised, and in changing from greyish-blue to red on the ninth day, it absorbed a larger amount of oxygen than during any other time of equal length. After sixteen days, it no longer contained any ferrous salt; the pink ferric salt into which it had changed had the formula, $Fe_2(OH)(HPO_4)(H_2PO_4)_3.4H_2O$. This formula is sup-

ported by its loss when heated, viz., 13·99 per cent. For a loss of $9H_2O$ from two molecules of such a salt, theory demands 13·75 per cent.

Dihydric ferrous phosphate is insoluble in alcohol, but when boiled with it for some hours, it is converted into a grey ferric salt of the formula $(Fe_2)_3(HPO_4)_3(PO_4)_4.12\frac{1}{2}H_2O$.

If air is not excluded when iron is boiled with excess of phosphoric acid, a green solution is obtained, from which a pink powder settles when it is allowed to remain over sulphuric acid. This powder is crystalline, and contains no ferrous iron. Its analysis leads to the formula $(Fe_2)_2(HPO_4)_5(H_2PO_4)_2$. When boiled with water it is converted into ferric phosphate, $FePO_4.2H_2O(Fe_2(2PO_4).4H_2O)$.

A reddish-grey powder consisting of microscopic prisms also separated out, of the formula $(Fe_2)_3(HPO_4)_6(PO_4)_2.7H_2O$.

Dihydroferric phosphate, $Fe_2(H_2PO_4)_6$, is obtained by dissolving ferric oxide in phosphoric acid until a precipitate begins to appear, then evaporating to dryness, and washing away the excess of phosphoric acid with ether. It is an anhydrous, pink, crystalline powder. When treated with a large excess of cold water, it gives a dirty yellow precipitate, which when dried has the formula—

$$(Fe_2)_4(PO_4)_6(HPO_4)_3.$$

When boiled with water it is converted into ferric phosphate, $Fe_2(PO_4)_2.4H_2O$.

Compound Ferric Phosphates.—Monodiferric phosphate—

$$Fe_2O_3(P_2O_5)_2(H_2O)_8,$$

is obtained by dissolving ferric phosphate in excess of phosphoric acid, and evaporating the solution over sulphuric acid. It forms small pink quadratic prisms, insoluble in cold water. When boiled with water it gives a white sandy powder, consisting of $Fe_2(PO_4)_3.4H_2O$. The relation between the mono-, the mono-di-, and the tri-ferric phosphate is thus shown:—

$Fe_2\{O.PO(OH)_2\}_6$ Monoferric phosphate.

$Fe_2\begin{cases} O.PO(OH)_2 \\ (O_2.POOH)_2 \\ O.PO(OH)_2 \end{cases}$ Mono-di-ferric phosphate.

$Fe_2\begin{cases} O_3.PO \\ O_3PO \end{cases}$ Triferric phosphate.

Di-triferric Phosphates.—By dissolving ferric hydrate in phosphoric acid of 48 per cent. in the proportion of $Fe_2O_3.14H_3PO_4$, and treating the product with 21 times its volume of cold water, a greyish-yellow precipitate was produced, of the formula $(Fe_2)_3(PO_4)_4(HPO_4)_3$. With boiling water the precipitate has the formula $(Fe_2)_4(PO_4)_6(HPO_4)_3$; and on boiling the filtrate from the last-mentioned salt, the substance which separates has the formula $(Fe_2)_4(PO_4)_4(HPO_4)_6$. If alcohol be added instead of water, the precipitate is white, and has the formula $(Fe_2)_4(PO_4)_2(HPO_4)_9$. This last salt has still the formula of a di-triferric phosphate, but is not far off the di-phosphate. Between the di-

and tri-ferric phosphates there appear to exist a large number of compounds.

Triferric Phosphate, $Fe_2(PO_4)_34H_2O$.—This compound can be prepared by boiling the monoferric-, or the mono-di-ferric phosphate with water, or by saturating phosphoric acid of 48 per cent. with ferric hydrate at the temperature of a water-bath. It forms a white granular powder, insoluble in acetic acid.

Phosphates of Aluminium.—*Mono-phosphate*, $Al_2(H_2PO_4)_6$. Prepared by dissolving aluminium hydrate in phosphoric acid in the proportion of $Al_2O_3 : 11H_3PO_4$, evaporating over a water-bath, and removing excess of phosphoric acid with ether. When viewed under the microscope this salt has the appearance of small prismatic crystals. It is deliquescent, and when its solution is allowed to stand for a long time, it deposits small triagonal and hexagonal plates. It is not decomposed by cold water, but when a dilute solution is boiled, it deposits tri-phosphate, $Al_2(PO_4)_3$.

Compound Phosphates.—(1). $Al_2(H_2PO_4)_4HPO_4.2H_2O$. By dissolving the triphosphate in phosphoric acid, and allowing the syrupy solution to remain over sulphuric acid for six weeks, it forms small hexagonal plates of the above formula. On treatment with cold water, it decomposes according to the equation, $[Al_2(H_2PO_4)_4HPO_4]_5 = [Al_2(H_2PO_4)_6]_3 + (Al_2)_2(HPO_4)_5(H_2PO_4)_2$. The latter salt is an indistinctly crystalline body, easily decomposed by boiling water.

Triphosphate, $Al_2(PO_4)_2 + 4H_2O$.—Easily prepared by boiling a dilute solution of the mono-phosphate. It is a white, indistinctly crystalline powder, having the above formula when dried over sulphuric acid in an exsiccator. W. R.

Double Salts of Calcium Sulphate. By R. Fassbender (*Deut. Chem. Ges. Ber.*, **11**, 1968—1970).—A double salt, having the composition $CaSO_4(KNH_4)SO_4 + Aq$, is obtained by adding an excess of potassium sulphate to a warm concentrated solution of ammonium sulphate which has been saturated with calcium sulphate. The same compound is formed when the double sulphate of calcium and potassium is treated with a warm solution of ammonium sulphate, and it can also be prepared by digesting calcium sulphate in a solution of potassium and ammonium sulphates. The corresponding sodium double salt could not be obtained.

The compound, $CaSO_4.K_2SO_42KCl.H_2O$, previously described by the author (*Ber.*, **9**. 1360) is found to be merely a mixture of potassium chloride and potassium calcium sulphate.

Calcium sulphate is deposited from a saturated solution of gypsum in common salt (on the addition of any salt which decreases its solubility), at the ordinary temperature, in the form of gypsum, but is precipitated as anhydride from boiling solutions. W. C. W.

Constitution of Ultramarine. By R. Rickmann (*Deut. Chem. Ges. Ber.*, **11**, 2013—2017). The author considers that in the conversion of ultramarine white, $2[Na_2Al_4(SiO_4)_2]Na_2S$, into ultramarine blue, by roasting with sulphur, the sulphurous acid combines with sodium and aluminium, liberating silicic acid, which in the nascent state unites

with sodium sulphide, forming sodium sulphosilicate, $S.Si(ONa)_2$, or "ideal ultramarine blue." W. C. W.

Constitution of Ultramarine. By A. Lehmann (*Deut. Chem. Ges. Ber.*, **11**, 1961—1968).—The conversion of green ultramarine into blue, which is slowly accomplished by the air or sulphurous anhydride, rapidly takes place on exposure to the vapour of sulphuric anhydride. Blue ultramarine is reconverted into green by fusion with sodium sulphate and charcoal. In this reaction, the sodium sulphide merely acts as a reducing agent, and does not combine with the ultramarine. The author proposes the following formulæ for ultramarines :—

White. Green.

$$2(Na_2S)_2S + 3Al_2Si_2O_7 \qquad 2(Na_2S)(Na_2O)S + 3Al_2Si_2O_7.$$

Blue.

$$2(Na_2O)_2S + 3Al_2Si_2O_7.$$

W. C. W.

Philippium. By W. G. Brown (*Chem. News*, **38**, 267).—While analysing sipylite, the solution of the earths occurring in connection with yttria was examined by means of the spectroscope, an absorption-spectrum of thirteen bands being obtained with great distinctness, whose positions were noted. To only two of these bands particular attention is drawn in this paper, one in the red, the other in the blue. The first was noted very faint; the second deep black. This latter line agrees with the characteristic line of philippium, and denotes in all probability the presence of that earth in sipylite. D. B.

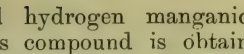
Remarkable Specimen of Silicon-iron. By J. L. Smith (*Chem. News*, **38**, 299).—This specimen of iron was picked up accidentally in a field near Louisville, Ky. When the author received it he concluded that it was a piece of a pig, having the form of the gutters into which the iron is run from the blast furnaces, with the raised borders. It was very brilliant, had a smooth surface, and on subjecting it to chemical analysis, it was found to resist almost every chemical agent except hydrofluoric acid, and fused soda or potash at a red heat. The colour of the mass is about that of platinum; sp. gr., 6·50; very brittle, being easily broken with the hammer; it is harder than ordinary pig, and somewhat vesicular in structure; fuses at about the temperature of cast-iron, and if heated to a little higher temperature in the air burns brilliantly. Its analysis gave :—Iron, 84·021; silica, 15·102; scaly graphite, 0·601; manganese, traces.

The accidental discovery of this mass (which is evidently a piece of a much larger mass) of silicon-iron is not without an important significance, for it demonstrates that iron can be produced on a large scale with a percentage of silicon that is very much greater than has been attained even in laboratory operations. D. B.

Potassium Permanganate and its Oxidation Products. By T. Morawski and J. Stingl (*J. pr. Chem.* [2], **18**, 78—95).—It is found that potassium permanganate easily gives up 6 atoms of oxygen, when it is either ignited, or is brought into contact in aqueous solution with oxidisable bodies, the precipitate which is produced being

a potassium and hydrogen manganic oxide, of the composition $Mn_4H_3KO_{10}$. This compound is obtainable also by digesting with potassium hydrate the compound $Mn_3H_4O_8$, prepared by the action of manganous chloride, $MnCl_2$, on potassium permanganate, and is identical with the compound which Rammelsberg obtained on treating with water the residue left on ignition of potassium permanganate.

Looking at the experimental results obtained, the authors consider that the formula of potassium permanganate is best expressed as follows:—



Oxidising Action and Products.—The action of *potassium permanganate on potassium sulphocyanide* in aqueous solution gave the insoluble body $Mn_4KH_3O_{10}$, and also potassium sulphate and cyanate, $3KCyS + 4K_2Mn_2O_8 + 3H_2O = 2Mn_4KH_3O_{10} + 3KCyO + 3K_2SO_4$.

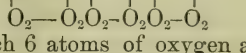
Action on Ethyl Alcohol.—The alcohol is oxidised to acetic acid, remaining in combination with the potassium to form potassium acetate, and the brown body above-mentioned is deposited, $2K_2Mn_2O + 3C_2H_6O = Mn_4KH_3O_{10} + 3(K.C_2H_3O_2)$.

Action on Oxalic Acid.—Complete oxidation to carbon dioxide and water, with formation of the brown precipitate, $Mn_4KH_3O_{10}$—

$$12H_2C_2O_4 + 4K_2Mn_2O_8 = 2Mn_4KH_3O_{10} + 3K_2CO_3 + 21CO_2 + 9H_2O.$$

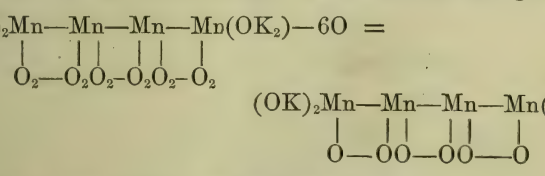
Action on Glycerin.—Complete oxidation takes place on applying a gentle heat, carbon dioxide and water being formed, and also the brown precipitate as before, $12C_3H_8O_3 + 28K_2Mn_2O_8 = 14Mn_4KH_3O_{10} + 21K_2CO_3 + 15CO_2 + 27H_2O$.

Thus the brown substance $Mn_4KH_3O_{10}$ is formed constantly, by the oxidation of various substances in aqueous neutral solutions; and calculating from the amount of oxygen given up in the above examples, *potassium permanganate yields up 3 atoms of oxygen easily in oxidation, if no free mineral acids be present, and the body* $Mn_4KH_3O_{10}$ *is formed.* This may be regarded as the salt of a *tetramanganic acid*, $H_4Mn_4O_{10}$, to make clear the formation of which it is considered advisable to write potassium permanganate as

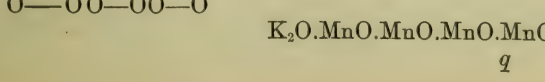


This formula explains the ease with which 6 atoms of oxygen are given up to an oxidisable body, without the presence of mineral acids, and also shows that with an acid (*e.g.*, SO_4H_2), 4 atoms more are given up.

(1.)



(2.)



$K_2O.MnO.MnO.MnO.MnO.K_2O.$

The body in equation (2) is evidently that obtained by Rammelsberg by igniting potassium permanganate.

By the action of manganous chloride on potassium permanganate, the body $Mn_3H_4O_8$ was obtained as a precipitate, and it is identical with that which Rammelsberg obtained by the action of concentrated sulphuric acid on the permanganate (*Ber.*, **8**, 233), $3K_4Mn_4O_{16} + 18MnCl_2 + 32H_2O = 12KCl + 24HCl + Mn_3H_4O_8$. The precipitate above mentioned, dried over sulphuric acid, yields the pure compound, but when heated at 100° it is decomposed as follows:—$4Mn_3H_4O_8 = 3Mn_4H_2O_9 + 5H_2O$. On boiling this compound, $Mn_3H_4O_8$, for a long time with potash or potassium carbonate, $Mn_4KH_3O_{10}$ is obtained. This body diffused in water, and boiled with barium chloride, filtered, and washed, furnished the compound $(Mn_4H_3O_{10})_2Ba$. Substituting silver nitrate for barium chloride, $Mn_4AgH_3O_{10}$ was obtained.

It is shown finally that the body obtained by Rammelsberg on igniting potassium permanganate, and decomposing the residue with water (which reaction he represents as $5K_2Mn_2O_5 = 2K_2Mn_5O_4 + 3K_2O$), really has the formula, $Mn_4KH_3O_{10}$. W. S.

Zinc Sulphydrate. By J. Thomsen (*Deut. Chem. Ges. Ber.*, **11**, 2044).—Zinc sulphate is completely precipitated by an equivalent of sodium sulphydrate, but if twice the quantity be added, a clear or slightly opalescent solution is obtained. This solution of zinc by sodium sulphydrate is analogous to that of the hydrated oxide by the alkalis. The author is about to publish the results of his investigation of the thermo-chemistry of this and other sulphides. C. F. C.

Composition of Precipitated Copper Sulphide. By J. Thomsen (*Deut. Chem. Ges. Ber.*, **11**, 2043).—A solution of copper sulphate is only slowly precipitated by the equivalent quantity of sodium sulphide; if twice this quantity be added, the precipitation is rapid and complete. The author has determined the composition of the precipitated sulphide, and finds that it is Cu_4S_3, and not CuS, as usually supposed; it is obtained mixed with free sulphur in the first case; in the second, the sulphur is dissolved by the excess of sodium sulphide, which it colours deep yellow. As regards the thermal aspect of the subject, the author finds that the formation of Cu_2S is attended by the evolution of 20,240 heat-units, but that the further fixation of sulphur by copper is marked by no appreciable heat manifestation. C. F. C.

Mineralogical Chemistry.

Breislakite. By H. v. Lasaulx (*Jahrb. f. Min.*, 1878, 380—383).—This mineral was first described by Brocchi (*Catal. di una raccolta di Rocce*, 1817), and classed with amphibole, but no reasons were given for this classification. Later, Monticelli and Covelli examined and described the breislakite from the lava of la Scala, near Naples (*Prodromo della mineralogia Vesuviana.* Napoli, 1825, p. 375), and

E. J. Chapman described a mineral from the lava of Capo di Bove, near Rome, which he considered to be breislakite, classing it with pyroxene (*Phil. Mag.* [3], **37**). The crystals described by Chapman were small and brilliant, and exhibited the following forms in combination, viz.: ∞P . ∝P∞ . ∞P∞ . ∞P∞ . P; the interfacial angles measured being as follows, viz.: P∞ : ∞P∞ = 106° 18′ P∞ : ∞P. = 100° 34′, and ∞P : ∞P = 87° 10′. Since that time (1849) breislakite has always been included in the pyroxene or augitic group of minerals. The author examined microscopically and optically the filiform breislakite from the lava of Capo di Bove, fine acicular breislakite from the lava of Vesuvius, and the reticulated felt-like variety from the trachyte of Solfatara, near Naples, and arrived at the certain conclusion that all these varieties of the mineral resemble amphibole very closely both in form and optical properties. The very fine acicular crystals from Capo di Bove and Vesuvius are very well developed and perfectly distinct under the microscope; the forms observed being ∞P. ∞P∞, with a very secondary modification of the clinodiagonal prismatic edge through ∞P∞, and occasionally P∞ . 0P. —P . 3P3. Measurements were obtained from sections at right angles to the vertical axis, which proved conclusively that the mineral was an amphibole. The inclination of 0P. to the vertical axis was carefully measured and ascertained to be 133¾°. An acute clinodome 2P∞ was noticed on some crystals and the angle of the inclination of the faces of this form to the vertical axis was found to be 60° on either side. The angle of 2P∞ : 0P in hornblende (amphibole) = 120° 52′. Twins were very common and easily recognised in polarised light, occurring sometimes with both terminals complete, and exhibiting all the characteristics of hornblende. A very careful and exhaustive optical examination of the varieties of breislakite already referred to showed that they belong most certainly to the amphiboles. The size of the crystals varied from ·009 mm. to ·09 mm., and all were trichromatic. The amount of material at the disposal of v. Lasaulx was not sufficient to allow of a quantitative analysis, but iron and manganese were detected by the blowpipe tests (a magnetic bead was obtained with great ease on fusing the breislakite before the blowpipe), whence he concludes that breislakite is a manganous-iron-amphibole, resembling closely the richterite from Pajsberg. C. A. B.

Phyllite, or Sericite-Gneiss. By C. W. Gümbel (*Jahrb. f. Min.*, 1878, 383—388).—The author examined the specimens in the museum of Chur, Switzerland, described by Theobald, under the name "Casanna-slates" (from the Casanna-Pass, south of Ponté), and at the first glance was of opinion that they were very closely allied to phyllite-gneiss.

Theobald named those slates which contained felspars, Casanna-slate. Gümbel found, on examining the slates from Casanna, that they occur associated intimately with the so-called "Bundener-slate." The typical Casanna slate from Davos, Spinabad, the Sertigthal near Dörfli, Stuls, Val Taors, the Alps d'Abbala, Campovosto in the Engadine, &c., were examined, and they exhibited without exception all the characteristics of phyllite or sericite-gneiss, the mica being re-

placed by sericite. An analysis of a portion of the sericite substance contained in a specimen from Val Taors, showed it to have a composition agreeing almost with that of the theoretical sericite of Lossen (*Zeitsch. d. Deutsch. Geol. Gesch.*; **19**, 547), as will be seen from the following, viz.: (No. 1 from Val Taors, Gümbel) (No. 2, Lossen) :—

No.	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.
1.	50·37	0·80	26·80	5·40	0·95	0·76	7·67	3·80	4·25=100·80
2.	51·06	—	25·21	8·83	—	—	11·56	—	3·34=100·00

A microscopical examination of the above-mentioned sericite was made, and the results showed it to be undoubtedly sericite. The author observed that the Casanna-slate in the form of phyllite-gneiss occurs almost exclusively in narrow bands enclosed in the older mica-gneiss, its occurrence in Bündener-slate being very rare.

A Hygrophilite-like Mineral from the "Rothelschiefer" of the Rhenish Palatinate.—The author found an embedded mineral of an intensely white colour disseminated in the upper strata of the "Rothliegenden" of the Palatinate at Reuschbach, east of Potzberg. This mineral appeared all the more prominent owing to its having a red back-ground. An analysis showed it to belong to the "clay-group," as will be seen from the following, viz.:—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
56·64	26·68	1·68	1·12	0·22	0·29	5·33	0·64	9·13 = 100·73

A comparison of the above percentage composition with that of the hygrophilite of Laspeyres, from the "Lower Rothliegenden," of the Harz shows that they are allied to each other, the composition of hygrophillite being as follows, viz.:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
48·42	32·05	3·26	1·15	1·72	5·67	1·36	9·02 = 102·65

The Reuschbach mineral has a sp. gr. of 2·415, and hygrophilite a sp. gr. of 2·670. As both the above-mentioned minerals occur in similar geological formations, the author considered it advisable to ascertain whether there existed an intermediate mineral in this formation; and in order to do this, he made a thorough examination of nacrite, lithomarge, pinite, and other minerals occurring in the "Rothliegegenden" of the coal-field of Saarbrück in the Palatinate. A white, soft mineral substance, with a greasy feel, occurring as a thin deposit on "slikensides" and clefts in the St. Ingbert mine was found to approach most closely to the new mineral. It contained very little alkali, and although its percentage composition agreed particularly with that of kaolin, its physical properties resembled those of nacrite; hence Gümbel classifies it with the latter mineral. A white mass occurring in clefts in the clay ironstone of Lebach was analysed and found to be almost identical with the typical nacrite of Vauquelin. The so-called "thonstein" or clay ironstone layers, occurring in the Rhenish Palatinate, were also examined and analysed, and found to vary much in composition. The author points to a fact which may

prove useful to porcelain manufacturers, viz.: "by levigating the "thonstein," a very plastic clay is obtained, which is refractory, and burns to an intensely white mass." An analysis was also made of the peculiar white or greyish massive hornstone-like mineral which occurs intimately associated with cinnabar, in the mines of Moschellandsberg, in the Palatinate (which the author proposes to name "hornthonstein"), and it was found to have nearly the same composition as the nacrite of Lebach. Gümbel promises further investigations into the relationship existing between the substances above referred to, and in the mean time does not feel justified in expressing a decided opinion as to the true position occupied by the mineral from Reuschbach. The analysis of No. 1, white mineral from St. Ingbert mine, No. 2, white mineral from the clay ironstone of Lebach, Nos. 2 and 4, thonstein from the "Rothliegenden," in the Palatinate, No. 5, "hornthonstein," from Moschellandsberg, are given below, viz.:—

No.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
1.	50·00	40·00	0·80	0·35	0·15	0·40	0·20	7·90	= 99·80
2.	46·92	37·50	2·52	0·09	0·12	0·27	0·14	13·16	= 100·72
3.	46·87	38·82	2·79	0·66	0·46	0·91	0·18	9·26	= 99·95
4.	64·08	25·62	0·52	0·06	0·03	0·14	0·02	9·52	= 99·99
5.	48·04	37·18	1·12	0·17	0·11	0·43	0·12	13·07	= 100·24

C. A. B.

A Simple and Sure Method of Detecting the Difference between Natural and Artificial Turquoise. By J. J. Pohl (*Jahrb. f. Min.*, 1878, 364—369).—The author does not include in his examination those so-called turquoises made by colouring ivory or other bone-material, but more particularly the close imitations of the natural mineral produced in Vienna, England, and France. These imitations possess all the characteristic physical properties of the natural stone in regard to colour, hardness, density, fracture, and appearance under the microscope; even the brown ferruginous enclosures (characteristic of the matrix of some inferior oriental turquoises) being added in some varieties, whilst a qualitative analysis simply shows the composition of the imitation to be almost identical with that of the true turquoise. The difficulty of discriminating between real and spurious turquoise is further increased by the fact of the former occurring in two distinct varieties, viz.: a blue and a green variety, which differ considerably in hardness, fracture, lustre, diaphanity, intensity of colour and chemical composition, &c., according to the locality from whence it came. Persian turquoise possesses mostly a pure sky-blue colour, and has an earthy appearance, whilst that from Germany, France, Nevada, and Mexico, has a greenish-blue to yellowish-green colour, with a slight lustre. The so-called "Egyptian or Alexandrian Turquoise," which has lately been brought into the market, equals the Persian variety in intensity of colour; in section, however, it appears paler, and fractured surfaces are more conchoidal than those observed on Persian turquoise. A further distinction between the two varieties is the greater brittleness of the Egyptian stone. The matrix of the Egyptian turquoise resembles closely that

of the other varieties, being a brown-red, strongly ferruginous granular quartz.

The author examined true turquoise from every known locality, together with numerous imitations. A quantitative analysis of the specimens is not of the slightest use, owing to the fact that the composition of true turquoise varies considerably, whilst the different tests hitherto recommended give untrustworthy results. The author recommends the following method, viz.: "A portion of the specimen to be tested is placed in a small covered platinum crucible and heated to redness over an ordinary Bunsen lamp, when a peculiar crackling noise (resembling that emitted by sodium chloride under similar circumstances) is heard after a few seconds; and on the lamp being taken away and the crucible opened, if the specimen be a *true* turquóise, a deep brown-black earthy powder or mass remains. When the specimen is an imitation turquoise, no crackling noise will be perceived on heating it, but the mass remaining will either fuse to blebby glass, or a solid hard body of a pure blue to greenish-blue colour, which is sometimes spotted here and there with brown-red on the surface, as though with cuprous oxide." C. A. B.

Preliminary Notes on the Analysis of the Zsadány Meteorite. By V. Wartha (*Zeitschr. Anal. Chemie*, 1878, 431—434).—The freshly fractured surface of this meteorite is rough and easily powdered, thus differing from that of the Knyalimyaer meteorite, which is hard, fine-grained, and very compact: the small tin-white particles of iron impart a slight steel-like lustre, which, however, disappears in a few hours in damp air, each iron particle being coated with ferric hydrate. Hence it is impossible to prepare a thin microscopical section: by means of a lens, however, there were found, besides iron and troilite, small white crystals, and a small non-metallic body, also detected by Kenngott in small quantity in the Knyalimyaer meteorite. The best means of isolating this black body consisted in covering the meteorite with 50 per cent. hydrochloric acid, and passing the vapour of hydrofluoric acid into the liquid: everything was thus dissolved except magnesium fluoride and the black body, and the latter was then readily isolated. It was in the form of shining octohedral crystals, and a blowpipe examination proved it to be picotite, a kind of chrome-ironstone.

For the mechanical examination of the meteorite, it was first finely powdered and then washed with alcohol until no coarse particles remained: the iron particles were then taken out with a magnet and subjected to a similar treatment as long as they yielded any mineral particles: the iron was not changed by this treatment. The coarse mineral particles were further examined to ascertain if mineral particles of different form were obtainable; by the examination of these the nature of the mixture may be determined.

The meteorite was examined for gases, by inclosing a portion in a strong glass tube, part of which was capillary; after exhaustion of the air, the electric spark was passed until the heat softened the glass. On examination of the light in the tube, a feeble hydrogen spectrum only was seen. The meteorite itself was unchanged, which proves

that the sulphur is present as ferrous sulphide and not as pyrites; this was confirmed by hydrogen sulphide being evolved when the powdered meteorite was rubbed with acid potassium sulphate. The Knyalimyaer meteorite yielded the same results, whence it is probable that the sulphur is in the form of troilite, and not of iron disulphide.

F. C.

Analysis of the Water of Thirlmere. By H. and C. Grimshaw (*Chem. News*, **38**, 216).—The samples of water analysed were taken by the authors above and below the narrow waist of the lake. The water was very clear and sparkling, practically free from sediment, and had a neutral reaction to litmus. From its analysis it will be seen that the water is one of the purest found in nature, not being surpassed by that of any locality in Great Britain, of which analyses have been published.

	Grains per gallon.		
	Lower sample.	Upper sample.	Roscoe.
Total solid matter	3·15	2·20	1·4500
Mineral matter	1·40	1·50	—
Loss on ignition	1·75	0·70	—
Total hardness	1·00	1·00	0·5000
Permanent hardness	1·00	1·00	0·5000
Chlorine	0·70	0·42	0·4200
Nitrogen as nitrates and nitrites	—	—	0·0247
Free ammonia	0·0021		—
Albuminoïd ammonia	0·0042		0·0049

D. B.

Mineral Spring, "Marienbunnen," near Iserlohn, Westphalia. By H. Vohl (*Deut. Chem. Ges. Ber.*, **11**, 1677).—An earlier determination gave 2·594 grams of solids in 16 ounces. Of this 0·427 gram consisted of acid ferrous carbonate, and the remainder of earthy sulphates and alkaline chlorides. The present sample tasted of iron salts, and its sp. gr. = 1·300569. 8004·544 grams left on evaporation 1·8945 gram residue, losing on ignition 0·2343 gram. 100,000 parts then, contain 23·688 parts of solids (at 100°), which consist of sodium oxide, 4·6889; potassium oxide, 0·0149; lime, 2·1468; magnesia, 1·0034; lithia, 0·0002; ferrous oxide, 2·0110; manganous oxide, 0·0108; silica, 0·1088; chlorine, 3·6660; bromine diodine, traces; sulphur trioxide, 3·1146; phosphorus pentoxide, traces; carbon dioxide, 3·5520; organic matter, traces. Water loss, 3·3710. Total = 23·6884. W. S.

Ofner Râdôczy-Bitterwater. By H. Vohl (*Deut. Chem. Ges. Ber.*, **11**, 1678).—The well was pumped empty, and after filling again, a sample was taken of the fresh water. Three sets of analyses are given of the water at different times in the course of two years (1876—1877), in order to show the fluctuations in the active mineral constituents. Sp. gr. at 15° R. = 1·04836. In 10,000 parts are—

	Moluar. 1876.	Tichborn. 1877 (beginning).	Vohl. 1877 (middle).
Magnesium sulphate ..	238·920	250·370	253·4480
Sodium „ ..	197·311	208·280	211·9640
Calcium „ ..	63·195	66·760	70·6600
Lithium „ ..	1·532	2·070	1·9890
Potassium „ ..	0·634	0·670	0·9760
Sodium chloride	21·680	23·140	27·5300
„ bromide.....	0·076	0·074	0·0788
„ iodide	—	—	0·0062
„ fluoride.....	—	trace	trace
„ carbonate	4·106	4·340	0·2933
Calcium carbonate....	6·611	7·000	1·2246
Ferrous carbonate....	0·509	0·539	0·4888
Alumina.....	0·484	0·270	0·3067 (phosphate)
Silica	0·260	0·516	0·5608
Ammonium sulphate..	—	0·703	—
Water and loss	—	—	1·8408
Total	535·318	564·733	571·3670

W. S.

Organic Chemistry.

Halogen Derivatives of Ethane and Ethylene. By W. Staedel (*Deut. Chem. Ges. Ber.*, **11**, 1735—1741).—I. *Carbon Hexchloride.* By E. Hahn.—Perchlorethane, C_2H_6 according to Regnault's observations, melts at 162°, and boils at 172°; later Geuther stated that the melting-point is 179°. The author finds that the freshly prepared chloride, formed by the action of chlorine on ethyl chloride, melts at 169°, and boils at 165—175°. This product when distilled yielded 5 fractions, boiling between 165° and 178°, which exhibited melting-points, varying from 117° to 173°. Each fraction, however, when crystallised from warm ether and alcohol, yielded a substance melting at 184°. In determining the boiling point of this body, it was observed that it sublimed, the author, therefore, made a series of observations under increased pressure. The description of the apparatus used in these experiments is to be published shortly. A sample of the chloride boiling at 185·5° under a pressure of 16·73 mm. above the normal, was found to melt at 183·5—184·5° (uncor.), or 187·51—188·43° (cor.). Similar experiments were made with a sample of perchlorethane, obtained from Kahlbaum; this preparation melted at 182°, and after crystallisation from ether yielded results similar to those already described. When perchlorethane is distilled under a slowly decreasing pressure, commencing with one 310 mm. above the normal atmospheric pressure, it appears that for every millimeter decrease in the pressure

there is a decrease of 0·054 in the boiling point; further, when the pressure is lowered, so that the boiling point should be 185°, the substance solidifies, showing that it boils at a lower temperature than that at which it melts. The melting point determinations made (I) by inserting the thermometer into a tube containing some of the chloride; (II) by the usual method, gave the following results:—I. 185—186° (uncor.); 181·71°—188·75° (cor.). II. 184·5—185° (uncor.); 186·85°—187·4 (cor.). The melted chloride may be slowly cooled to 120°, when it solidifies to a transparent mass; this when heated to a little below its melting point, becomes opaque.

II. *Chlorobromo- and Bromo-substitution Products of Ethane and Ethylene.* By J. Denzel.—Bromine acts on ethyl chloride in sunlight, yielding several products. (1.) *α-Chlorobromethane*, $CH_3.CHBrCl$.—This is a mobile liquid, having a pleasant odour resembling that of chloroform, and a sweet taste; it is but slowly attacked by alcoholic potash. Its boiling point is 84—84·5° (bar. 744 mm. at 15°), and at 16° it has a sp. gr. 1·666. (2.) *α-Chlorodibromethane*, $CH_3.CBr_2Cl$. A mobile liquid having an odour like turpentine. It boils at 123—124° (bar. 753 mm. at 16°); its sp. gr. is 2·134 at 16°. Alcoholic potash reacts with this substance, after standing with it for a quarter of an hour. (3.) *β-Chlorodibromethane*, $CH_2Br.CHBrCl$. This is a colourless liquid, boiling at 162·5—163°, having an odour less agreeable than that of the α-compound, and has a sp. gr. 2·268 at 16°. Alcoholic potash reacts immediately with this compound. (4.) *α-Chlorotribromethane*, $CH_2Br.CBr_2Cl$. A liquid boiling at 200—201° (bar. 735 mm. at 14°) with partial decomposition. The distillate is slightly coloured, but is rendered colourless by exposure to light. It boils at 170—171° under a pressure of 335 mm., and at 165—167° under 285 mm. Its sp. gr. is 2·602 at 16°. Alcoholic potash acts immediately on this and the more highly brominated products. It does not solidify when cooled to −20°, nor do the compounds already described. (5.) *α-Chlorotetrabromethane*, $CHBr_2.CBr_2Cl$, is a colourless, crystalline solid, melting at 32—33°; it boils at 200—201°, under a pressure of 285 mm. At 16° its sp. gr. is 2·366.

When bromine acts upon ethylidene chloride the following compounds are formed:—(1.) *α-Dichlorobromethane*, $CH_3.CBrCl_2$. A clear, colourless, mobile liquid, boiling at 98—99° (bar. 758 mm. at 16°). It has a sp. gr. of 1·752 at 16°. It is but slowly acted upon by alcoholic potash. (2.) *α-Dichlorodibromethane*, $CHBr_2.CBrCl_2$, is obtained by distillation as a yellow liquid boiling at 176—178°. It is decolorised by the action of light, and has at 16° a sp. gr. of 2·27. (3.) *α-Dichlorotribromethane*, $CHBr_2.CBrCl_2$, an oily liquid, boiling at 215—220°, and, like the two other compounds, remaining liquid at −20°. *α-Chlorobromethylene*, $CH_2{=}CBrCl$, is obtained by treating α-dichlorobromethane or β-chlorodibromethane, with alcoholic potash. It is a colourless liquid boiling at 62—63° (bar. 750 mm. at 18°) and readily undergoes polymerisation, forming a white, amorphous powder. *α-Chlorodibromethylene*, $CHBr{=}CBrCl$, is obtained from α-chlorotribromethane, in a manner similar to α-chlorobromethylene. It is a colourless liquid, of sp. gr. 2·275 at 16°, and boiling at 141—142°.

Like the last described compound, it attacks the eyes, but less energetically.

α-Dichlorobromethylene, $CHBr{=}CCl_2$, is obtained in a similar manner from α-dichlorodibromethane. It is a colourless liquid, which boils at 114—116° (bar. 740 mm. at 17°), and has a sp. gr. of 1·906 at 16°. Like the two other ethylene derivatives, it remains liquid when cooled to −20°. *α-Dichlorodibromethylene*, $CBr_2{=}CCl_2$, boils at a temperature above 160°, and remains liquid at −20°.

α-Dibromethane, $CH_3.CHBr_2$, a liquid boiling at 109—110° (bar. 750 mm. at 13°), and *α-tribromethane*, $CH_3.CBr_3$, boiling at 187—188° (bar. 721 mm. at 15°), are formed by the action of bromine on ethyl bromide. P. P. B.

Diethylallyl Carbinol. By A. Saytzeff and Schirokoff (*Deut. Chem. Ges. Ber.*, **11**, 2153).—The above alcohol was prepared by the action of zinc on a mixture of diethylketone and allyl iodide. It forms addition-products with bromine, and is oxidised by chromic acid to diethylketone and carbonic, acetic, and propionic acids. C. F. C.

Action of Sulphuric Acid (dilute) on Allyldimethyl and Allyldipropyl Carbinols. By A. and P. Saytzeff and W. Nikolsky (*Deut. Chem. Ges. Ber.*, **11**, 2152—2153).—By the action of dilute sulphuric acid on allyldimethylcarbinol, the authors have obtained the hydrocarbons, C_6H_{10} and $C_{12}H_{20}$, whilst allyldipropylcarbinol yields the hydrocarbon, $C_{10}H_{18}$, only. On the supposition that the formation of $C_{12}H_{20}$ is analogous to the conversion of trimethylcarbinol into diisobutylene, the authors assign to it the constitutional formula,

$$(CH_3)_2.C{=}C(CH{=}CH_2).C(CH_3)_2.CH_2.CH{=}CH_2,$$

regarding it further as closely related in structure to the terpenes. In these latter compounds they deny the existence of the aromatic nucleus as such, although their structure is such as to admit of their ready formation by simple reactions. The following constitutional formula is proposed for $C_{10}H_{16}$:—

$$CH_2{=}CH.CH_2.CH{=}C(CH{=}CH_2).CH(CH_3)_2,$$

as indicating its close relationship both to the aromatic and to the fatty hydrocarbons. Its possible formation from isobutylene, in a manner similar to that of diisobutylene, will be evident.

C. F. C.

Etherification of Secondary Alcohols. By N. Menschutkin (*Deut. Chem. Ges. Ber.*, **11**, 2117—2120).—Of the results of this investigation of the rate of etherification of certain secondary alcohols, which are given in the tabular form, the following are the more important. With alcohols of similar structure, the initial velocity (V) is greatest in the case of the lowest member of the series, diminishing until it reaches a point where it remains constant for the higher members. Thus we have the following values of V:—

Dimethyl carbinol	26·53
Ethylmethyl carbinol	22·59
Hexylmethyl carbinol	21·19

Smaller values are observed for secondary alcohols of different structure. Thus for

Isopropylmethyl carbinol	19·95
Diethyl carbinol.....	16·93

the initial velocities of the primary differ from those of the secondary by 20—30 per cent. After the first hour the velocity is greater for the secondary.

The relative values of V diminish with increase of molecular weight. Thus :—

Dimethyl carbinol	48·35
Ethylmethyl carbinol	38·10
Hexylmethyl carbinol	34·16

The influence of isomerism upon the relative values of V is also evident. Thus :—

Isopropylmethyl carbinol	31·95
Diethyl carbinol	28·86

The relative initial velocities of the primary differ from those of the secondary alcohols by about 30 per cent. The influence of the composition of the alcohols upon both values of V is equally evident in the case of those containing unsaturated groups. Thus the absolute value for

Ethylvinyl carbinol	14·85
Diallyl carbinol	10·60

The relative values for

Ethylvinyl carbinol	28·42
Diallyl carbinol	21·14

The following are the limiting values observed for secondary alcohols $C_nH_{2n-1})_2.CH(OH)$:—

Dimethyl carbinol	60·52
Ethylmethyl carbinol	59·28
Isopropylmethyl carbinol.....	59·31
Diethyl carbinol.....	58·66
Hexylmethyl carbinol	62·03

These differ from the corresponding values for the primary alcohols by 6—10 per cent.

A lower limit is observed for alcohols with the same number of carbon atoms, but containing unsaturated affinities. Thus for

Ethylvinyl carbinol	52·25
Diallyl carbinol	50·12

C. F. C.

Etherification of Tertiary Alcohols and Phenols. By N. Menschutkin (*Deut. Chem. Ges. Ber.*, **11**, 2148—2151).—The study of the etherification of the tertiary alcohols is complicated by the formation of hydrocarbons, the molecular ratio of unity between the water and ether formed, observed in the case of the primary and

secondary alcohols being therefore also disturbed. The data furnished by the author's investigation of the etherification of trimethylcarbinol by acetic acid (in which isobutylene is formed) at 154°, prove that the limit of the decomposition is expressed by the equation, $11C_2H_4O_2 + 11C_4H_{10}O = 10C_2H_4O_2 + 4C_4H_{10}O + C_2H_3(C_4H_9)O_2 + 6C_4H_8 + 7H_2O$. The limit observed under these abnormal conditions must at the same time be less than the normal one. A nearer approximation is attained at 100°, the limit at this temperature being expressed by the equation, $16C_2H_4O_2 + 16C_4H_{10}O = 14C_2H_4O_2 + 11C_4H_{10}O + 2C_2H_3(C_4H_9)O_2 + 3C_4H_8 + 5H_2O$. It follows from the difference thus observed that the ethereal salt in question is decomposed on heating. Similar abnormal results were obtained in the etherification of other tertiary alcohols.

In addition to the decomposition of the ethereal salts into acid and olefines, which it is to be observed is aided by the relatively large mass of water present, the reaction is probably further complicated by the reunion of the olefine and water. The following were observed at 154° as the limits for—

Trimethyl carbinol	6·59
Ethyldimethyl carbinol	2·53
Diethylmethyl carbinol	3·78
Propyldimethyl carbinol.....	0·83
Isopropyldimethyl carbinol	0·85

These numbers are not comparable with those obtained with the primary and secondary alcohols for the reasons explained; the initial velocities of all classes are however strictly relative, since in the etherification of the tertiary, no hydrocarbon was formed during the first hour. The following were observed as the initial velocities for—

Trimethyl carbinol	1·43
Ethyldimethy carbinol	0·81
Diethylmethyl carbinol	1·04
Propyldimethyl carbinol.....	2·15
Isopropyldimethyl carbinol	0·86

Tertiary alcohols containing unsaturated affinities present similar phenomena.

The following were the limits for—

Allyldimethyl carbinol	7·26
Allyldiethyl carbinol	4·72
Allyldipropyl carbinol.....	0·46
Diallylmethyl carbinol	5·36
Diallylpropyl carbinol.....	3·10

In all cases it will be seen that the limiting values are diminished *pari passu* with the complexity of the substituting groups; and on comparing the alcohols containing unsaturated affinities with those of the series $C_nH_{2n-1}OH$, the limit is found to be lower the smaller the number of unsaturated affinities, *i.e.*, the converse of what was observed for the primary and secondary alcohols.

The following were observed as the initial velocity and limit of etherification respectively for the phenols:—

	Initial velocity.	Limit.
Phenol	1·45	8·64
Paracresol	1·40	9·54
Thymol	0·55	9·46
α-Naphthol	—	6·16

The etherification of the phenols is normal. C. F. C.

Action of Potassium Cyanate on Epichlorhydrin. By A. L. Thomsen (*Deut. Chem. Ges. Ber.*, **11**, 2136—2139).—Epichlorhydrin was boiled with a solution of potassium cyanate in a flask attached to an inverted condenser. On subsequent evaporation, the solution yielded well formed colourless prisms of a compound, $C_4H_6NClO_2$, formed therefore by the direct addition of a molecule of cyanic acid to epichlorhydrin.

It is a stable compound, resisting decomposition by hot concentrated hydrochloric acid (at 100°), and by water under pressure at 150°. At this temperature, however, it is decomposed by hydrochloric acid, with formation of carbonic anhydride, ammonium chloride, and other bodies. It is similarly decomposed by potash and by aqueous ammonia.

Heated with acetic anhydride at 180°, it yields a crystalline aceto-compound, $C_6H_8NClO_3$ (m.p. 79°). This observation increases the probability of the presence of an NH-group in the original compound. By the action of aniline at 170° upon the latter, it is converted into carbanilide, and a compound which is still under investigation.

C. F. C.

Reduction of Cupric Oxide (Fehling's Solution) by Milk Sugar. By H. Rodewald and R. Tollens (*Deut. Chem. Ges. Ber.*, **11**, 2076—2084).—In this investigation, the authors employed two solutions, viz., of 60 grams NaOH, and 173 grams $KNa.C_4H_4O_6$ to 500 c.c., and of 34·639 grams $CuSO_4$, also dissolved to 500 c.c., which were mixed in equal volumes just previous to use. The cuprous oxide was collected on a small asbestos filter (Soxhlet's method), and estimated as metal, after reduction by hydrogen. The following are the results of this investigation as regards the influence: (1) Of time.—The decomposition is invariably complete after four minutes' boiling of the solution. (2) Dilution of the solution.—1 mol. crystallised milk-sugar, $C_{12}H_{22}O_{11}.H_2O$, decomposed by a slight excess of the Fehling's solution (160 c.c. to 1 gram), precipitated a number of atoms, Cu (as Cu_2O), varying with the degree of dilution from 7·34 when diluted with an equal volume of water, to 7·53 when 4 vols. water were added. An explanation of this lies in the probability of a specific action of the alkali on the sugar, which would be greater the greater the concentration of the solution. (3.) Excess of Fehling's solution.—This causes a greater precipitation, proportional, within limits, to the excess. A number of titration experiments, in which the sugar solution was added with varying rapidity, until the copper was completely

precipitated, showed that more was required, the more rapidly it was added.

Strictly accurate results, by titration alone, can be obtained only by keeping these factors constant. For this purpose it is necessary to know, approximately, the quantity of sugar present in a solution under investigation, and for every gram to add 160 c.c. of Fehling's solution, and so much water (in addition, if necessary) that the latter is in a condition of 3—4 fold dilution at the end of the operation. It is then further necessary to repeat the titration, adding at once in the second the number of c.c. that were used in the first for complete precipitation, and similarly with a third titration, which will give the final result. The solution is standardised by an experiment under these standard conditions, controlled by a gravimetric estimation.

C. F. C.

Nitro-compounds of Cellulose. By G. Wolfram (*Dingl. polyt. J.*, **230**, 45—53).—A large number of experiments and analyses made with pyroxylin (gun cotton) showed that it differed essentially from xyloïdin prepared from starch, but up to the present time a certain amount of doubt exists as to the proper formula of pyroxylin. Pelouze gives it as $C_{24}H_{17}O_{17}(NO_5)_5$*; Schönbein and Böttger $C_9H_6N_2O_{13}$; Peligot $C_{24}H_{18}X_6O_{24}$; Schmidt and Hecker $C_{24}H_{16}X_5O_{21}$; van Kerkhoff and Reuter $C_{24}H_{13}X_6O_{19}$; Porret and Teschemacher $C_{24}H_{16}X_8O_{24}$; Domonte and Ménard $C_{24}H_{18}X_6O_{24}$ and $C_{24}H_{16}X_4O_{20}$; the former soluble, the latter insoluble, in ether-alcohol. According to Hadow, three compounds are obtained by treating cotton with nitro-sulphuric acid of various concentration:—

a. $C_{12}H_7X_3O_{10}$, or $C_{36}H_{21}X_9O_{30}$; insoluble in ether-alcohol.
b. $C_{36}H_{22}X_8O_{30}$; soluble in ether-alcohol.
c. $C_{36}H_{23}X_7O_{30}$; soluble in ether and in glacial acetic acid.

The author nitrated cellulose (cotton, hemp, paper, linen, straw) in various ways, and investigated the products formed, with a view of solving the uncertainty which prevails as to the composition and the number of nitro-compounds of cellulose, and further to show what influence various acid mixtures have on cellulose under various conditions. The sulphuric acid used in these experiments had a sp. gr. of 1·8424. The concentration of the nitric acid was in one series of trials equal to 1·38 sp. gr., in another 1·505. By mixing the two acids, an increase of temperature to 60—80° was occasioned. After cooling the mixture to the desired temperature, the cellulose was added, and left to itself for about 24 hours at a temperature of 20—23°. The nitro-cellulose was then washed very carefully, and dried either in a vacuum or in the air. The compounds analysed were compared with one another by their percentage of nitrogen tetroxide. By regarding trinitrocellulose, or when doubled hexanitrocellulose, as the highest stage of nitration, the following six compounds would be possible:—

* In all these formulæ $C = 6$, $O = 8$, and $X = NO_5$.

$C_{12}H_{19}O_{10}NO_2$, mononitrocellulose, with 12·49 per cent. NO_2.
$C_{12}H_{18}O_{10}.2NO_2$, dinitrocellulose, ,, 22·22 ,, ,,
$C_{12}H_{17}O_{10}.3NO_2$, trinitrocellulose, ,, 30·06 ,, ,,
$C_{12}H_{16}O_{10}.4NO_2$, tetranitrocellulose, ,, 36·50 ,, ,,
$C_{12}H_{15}O_{10}.5NO_2$, pentanitrocellulose, ,, 41·89 ,, ,,
$C_{12}H_{14}O_{10}.6NO_2$, hexanitrocellulose, ,, 46·76 ,, ,,

D. B.

Decomposition of Ethyl Disulphoxide by Potash. By C. Pauley and R. Otto (*Deut. Chem. Ges. Ber.*, **11**, 2073—2075).—According to Löwig and Weidmann (*Pogg. Ann.*, **49**, 323) ethyl disulphoxide yields on treatment with potash, ethyl disulphide, alcohol, and the potassium salt of "Doppelt-Schwefeläthylschwefelsäure." This decomposition appears therefore to differ essentially from that which the authors have found to occur with the aromatic disulphoxides; they have subjected it to a careful investigation, the result of which is to show that it takes place according to the equation—

$$\underset{\text{Ethyl disulphoxide.}}{2(C_2H_5)_2S_2O_2} + H_2O = \underset{\text{Ethyl disulphide.}}{(C_2H_5)_2S_2} + \underset{\text{Ethylsulphonic acid.}}{C_2H_5.HSO_3} + \underset{\text{Ethylsulphinic acid.}}{C_2H_5.HSO_2}$$

and is therefore uniform with, and not different from those of benzene and toluene disulphoxides; and that ethyl disulphoxide is therefore also thio-ether, $C_2H_5.S.C_2H_5SO_2$. This view is in harmony with its decomposition by zinc into ethylsulphinate and sulphydrate (*i.e.*, zinc-compounds of these: $\left.\begin{matrix}2C_2H_5SO_2\\C_2H_5\end{matrix}\right\}S + Zn_2 = (C_2H_5.SO_2)_2Zn + (C_2H_5S)_2Zn$,
which is also uniform with those of the aromatic disulphides by zinc (*Ber.*, **11**, p. 2070). C. F. C.

Formation of Ethylamine. By H. Köhler (*Deut. Chem. Ges. Ber.*, **11**, 2093—2095).—Mercurous amidochloride heated in a stream of ethyl chloride, yields ethylamine in small quantity, probably according to the equation: $NH_2Hg_2Cl + C_2H_5Cl = Hg_2Cl_2 + NH_2.C_2H_5$. Mercuric amidochloride appears to be similarly decomposed: $NH_2.HgCl + C_2H_5Cl = HgCl_2 + NH_2.C_2H_5$. Ethylamine was also obtained by the author by the action of dry ammonia on sodium ethylate, in quantity equal to 5 per cent. of the sodium employed; and further, in similar quantity by heating together ammonium chloride and sodium ethylate.
C. F. C.

Formation of Methyl Aldehyde. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, **11**, 1685).—If the vapours of the well-known "lamp without flame," fed with methyl alcohol, be condensed, a fluid is obtained containing never more than 1 per cent. of methyl aldehyde. The estimation was made by converting the aldehyde into the sulphur-compound. To get a more concentrated aldehyde solution, a suitable mixture of methyl-alcohol vapour and air was passed through a platinum tube containing a quantity of thin platinum wires. On gently warming, streams of methyl aldehyde were obtained, and condensed to a liquid containing not less than 5 per cent. of the aldehyde. Properly set up and arranged, such an apparatus can be kept going for months

without intermission. The methyl alcohol was removed from the aldehyde solution by distillation, and the residual liquid was frozen repeatedly, the ice being removed. In this manner the amount of aldehyde was increased to 10 per cent. and more. W. S.

Diethylglyoxylic Ether and Diethylglyoxylamide. By A. Geuther (*Deut. Chem. Ges. Ber.*, **11**, 1093).—The author reminds Pinner, relatively to his recently published observation of the formation of the above compounds by the action of hydrochloric acid and hydrocyanic acid on alcohol, that Schreiber, as long as eight years ago, prepared these same compounds from dichloracetic acid.

C. F. C.

Formation of a Ketone containing Four Carbon-atoms from Dibromethylene. By E. Demole (*Deut. Chem. Ges. Ber.*, **11**, 1710—1715).—In a former communication (this Journal, 1878, 847) the author assumes the existence of an unsaturated molecule, C_2HBr, to account for the oxidation and polymerisation which $C_2H_2Br_2$ undergoes. In the hope of obtaining this body, dibromethylene was submitted to the action of hypobromous acid, which by oxidising $C_2H_2Br_2$ would liberate C_2HBr, and this would probably form a compound with HBrO. The result of the action is, however, that some bromacetic acid is formed from the oxidation of the $C_2H_2Br_2$, and at the same time an oily liquid is obtained. This, on exposure at 100° for some time, leaves a residue, which, after crystallisation from alcohol forms large prisms grouped together in bunches; they melt at 89—90°, and decompose when heated above 100°. This compound, which has the composition $C_4H_2Br_6O$, is insoluble in cold water, slightly soluble in cold alcohol, more so in hot, and dissolves easily in ether. It is not acted on by bromine or by acids, and but slowly by alcoholic potash, nor does acetic chloride or anhydride attack it; hydroxyl-groups are therefore absent.

The alcoholic solution of $C_4H_2Br_6O$, when reduced with sodium amalgam in a current of hydrochloric acid gas, yields ethylmethyl ketone, C_4H_8O (b. p. 79—81). The formation of this compound shows that $C_4H_2Br_6O$ is hexbromethylmethyl ketone.

When $C_4H_2Br_6O$ is oxidised with nitric acid, malonic acid, $C_3H_4O_4$, is obtained, together with carbonic anhydride and bromine. The formation of malonic acid (m. p. 139—140°) shows that the ketone $CBr_3.CO.CH_2.CBr_3$, is oxidised in accordance with Popoff's law.

The formation of the hexbromethylmethyl ketone is explained as follows:—

(1.) $2C_2HBr + BrOH = CBr_2.CH(OH).CH.CBr.$

(2.) $CBr_2.CH(OH).CH.CBr + HBr + Br_2 = CBr_3.CH(OH).CH_2.CBr_3.$

The secondary alcohol so formed is converted into the ketone, as the group CH(OH) could not exist attached to so many bromine atoms, and is therefore changed to the group CO. P. P. B.

Decomposition of Ethyl Mono-, and Dibrom-acetates. By F. Kepel (*Deut. Chem. Ges. Ber.*, **11**, 2115—2117).—Ethyl dibromacetate

is rapidly and quantitatively converted into dibromacetamide by agitating it with six times its volume of 20 per cent. ammonia until the whole becomes solid. Monobromacetamide is similarly obtained from the corresponding ether, but only when the reaction takes place at a low temperature (0°). This body is easily soluble in water, slightly so in alcohol, almost insoluble in ether. At a higher temperature traces only of monobromacetamide are formed, the products of the reaction being ammonium bromide and acetate. C. F. C.

Diazo-Compounds of the Fatty Series. By W. Zorn (*Deut. Chem. Ges. Ber.*, **11**, 1630—1634).—Nitrosyl-silver, AgNO, acts with great energy on ethyl iodide, so as to cause explosions, if the materials are not previously diluted. The iodide should be diluted with ether, and the silver salt with sand, and only small quantities operated on at a time. The product of the reaction is a colourless oil, insoluble in water, on which it forms a layer. It has an ethereal odour, not at all unpleasant, a neutral reaction, and is not soluble in hydrochloric acid or soda solution. It is almost as explosive as nitrogen chloride. Rise of temperature (in one case to 45°), and a blow, or even slight concussion, will cause it to explode. The combustion was effected by placing the substance in a little weighed glass apparatus outside the combustion-tube, and passing the vapour of it into the tube by means of a current of air, nitrogen, or carbonic anhydride. The vapour density was taken by the improved Hofmann's method, in carbon bisulphide vapour and in methyl acetate vapour. Mean vapour-density = 4·04. The rational formula was therefore $2(C_2H_5NO)$. On reduction with tin and hydrochloric or glacial acetic acid, or with sodium amalgam, nitrogen gas was evolved, $(C_2H_5)_2N_2O_2 + H_2 = N_2 + 2C_2H_5.OH$; so that the body cannot be a nitroso-compound (or most probably ethylamine would have been formed). The body is also not a hyponitrous ether, for potash solution and alcoholic potash are alike without action upon it. Water decomposes it at ordinary temperatures, and very quickly at 40°, with evolution of pure nitrogen. Efforts to make determinations by measuring the gas evolved in the decomposition just mentioned were not crowned with success, as more or less bye-products were also formed, according to the temperature employed, the decomposition being $(C_2H_5)_2N_2O_2 + H_2O = N_2 + CH_3.COH + C_2H_5.OH + H_2O$. The whole behaviour is thus seen to be that of a *diazo-compound*, which may be thus written:

$$C_2H_5.O.N{=}N.O.C_2H_5,$$

and it is named *diazoethoxane*. It is remarked that the body may also be compared with the diatomic ether, $C_2H_5O.C_2H_4.C_2H_5O$, and may be written $C_2H_5O.N_2.C_2H_5O$, and be named diazo-ether. In outward form there is great resemblance between this formula and that of an azo-compound, but its properties are quite different. W. S.

The Volatile Acid of Croton Oil. By E. Schmitt (*Arch. Pharm.* [3], **13**, 213—229).—Schlippe (*Annalen*, **105**, 1) states that besides crotonol, $C_9H_{14}O_2$, stearic, palmitic, lauric, myristic, and oleic acids, also crotonic, angelic, and other higher acids of the acrylic-acid series, are to be found in croton oil, combined with glycerin: whereas

Geuther and Fröhlich (*Zeits. Chem.*, 1870, 26 and 549) state that a liquid acid of the formula $C_4H_6O_2$ is to be found in the oil, nor can the solid acids therein contained be identified with angelic acid, but that the liquid volatile acids are acetic, butyric, and valeric acids also a small proportion of œnanthylic acid, and perhaps other higher members of the oleic acid series. Although the solid acid has the composition of angelic acid, it is not identical therewith, but merely isomeric, as it melts at 64°, whereas angelic acid melts at 45°. Geuther and Fröhlich have named this acid *tiglic acid*, and consider that it is probably identical with Frankland and Duppa's methylcrotonic acid, as the ethylic ethers of both acids boil at 156°, and the melting-points differ by only 2°; they find, however, that the odours of the two acids are different, and that the barium salt of methylcrotonic acid crystallises in a vacuum anhydrous, whereas the barium salt of tiglic acid has the formula $C_5H_7O_2ba + 5Aq$. To ascertain the cause of these discrepancies the author saponified 20 pounds of croton oil, and after separating the solid soap, decomposed the brown mother-liquid with sulphuric acid, and distilled to separate the volatile acids. The distillate was then neutralised with soda, and after evaporation decomposed by sulphuric acid, and the separated acids dissolved in ether. The acids dried and submitted to fractional distillation gave distillates at 160°, 160—190°, 190—205°, 205—270°.

The tiglic acid which was contained in the fraction 190—205° was then crystallised out by the aid of a freezing mixture. Compared with that obtained by Geuther the yield of this acid was small, whereas that of the acids of lower boiling-point was larger; in fact it was found that, although the yield of volatile acids was nearly constant in all cases, the amount of the different acids present was in no constant proportion. To separate the remaining acids, the distillates were dried with anhydrous phosphoric acid, and re-distilled. The fractions collected at 115—125°, 150—160°, 168—178°, in all amounting to 15—20 grams, were the only important fractions, the remainder being insufficient for examination; propionic acid therefore was absent, or at any rate only traces were present. On applying Liebig's method of partial neutralisation to each of the above fractions, the author was enabled further to separate by distillation the acids contained in those fractions. In the first, formic and acetic acids were found; in fraction 150—160° isobutyric acid; in the third fraction 168—170°, valeric acid, contaminated with a small quantity of tiglic acid. Methylcrotonic acid. prepared according to Frankland's method, was compared with tiglic acid, and the two were found to be identical; they both crystallise in well-formed tables, having a benzoïn-like odour; in crystalline form, angles, and optical properties identical; soluble with difficulty in cold, but easily in hot water; they melt at 64°, and boil at 196—197°. The ethylic ethers of both acids boil at 154—156°, and the barium salt has the formula $(C_5H_7O_2)_2Ba + 4Aq$.

Like methylcrotonic acid, tiglic acid is decomposed when fused with potash into acetic and propionic acids with evolution of hydrogen, but nascent hydrogen has no effect on these acids. By treatment with fuming hydriodic acid, a solid acid melting at 86·5° is obtained, which

appears to be isomeric with iodovaleric acid ($CH_3.C_2H_4C.COOH + HI = CH_3.C_2H_5CI.COOH$).

In the same manner as angelic acid is converted into valeric acid by the action of hydriodic acid and amorphous phosphorus (Ascher, *Ber.*, **2**, 685), methylcrotonic acid yields valeric acid. With bromine also it yields a dibrominated addition-product ($CH_3.C_2H_4Br.CBrCOOH$), which melts at 82—83°.

Concerning the substances contained in the fractions boiling above 200° nothing definite has been ascertained, as the amount was small, but they are probably members of the oleic series. E. W. P.

Action of Ethyl Iodide on the Silver Salts of Maleic and Fumaric Acids. By R. Anschütz (*Deut. Chem. Ges. Ber.*, **11**, 1644—1646).—Those derivatives are wanting in the maleic series which are known in the fumaric series. Of *fumaric acid*—chloride, diethylether, imido-compound, *known;* anhydride, *unknown;* whilst of *maleic acid*—chloride, diethylether, imido-compound, *unknown;* anhydride, *known*. The object of this research is to complete these two series of derivatives. The first attempt was to obtain the fumaric and maleic diethyl-ethers.

The ethyl fumarate has been obtained both from maleic acid and from fumaryl chloride (Laubenheimer, *Annalen*, **164**, 294), (b. p. 218°). The silver fumarate and maleate were treated with excess of ethyl iodide at ordinary temperatures: in this way exactly the same ethyl salt was obtained from both acids. The two samples had the same odour, and both boiled at 218·5°, the same sp. gr., and gave the same saponification-product, namely, fumaric acid. If it can be shown that the hitherto so-called diethyl fumarate is only in fact diethyl maleate, then the conclusions as to the molecular magnitude of the fumaric derivatives drawn from the vapour-density determination by Hübner and Schreiber, would fall beside the mark (*Gött. Nachrichten*, 1872, 329).

The author intends to examine other methods of preparing the neutral maleic ethers, and other ethereal saponification methods. It is proposed also to prepare the benzoyl- and acetyl-tartaric ethers from both the dibromsuccinic ethers by treatment with silver benzoate and acetate respectively (only the ethyl salt of ordinary dibromosuccinic acid is known), so as to observe if identical tartrate-derivatives be obtained from both dibromo-acids or not. W. S.

Racemic Acid. By W. Staedel (*Deut. Chem. Ges. Ber.*, xi, 1752—1753).—Racemic acid forms crystals of the formula $C_4H_6O_6 + H_2O$, belonging to the triclinic system, and disintegrating on exposure to air. Artificial racemic acid made according to Strecker's reaction (*Zeit. f. Chem.*, 1868, 216) may be obtained by crystallisation from water in crystals having the same form as those from the natural acid, but which do not disintegrate. Further, the anhydrous racemic acid melts at 201°, whilst that synthetically prepared melts at 198°.

When racemic acid is converted into the sodium ammonium salt, the first crystals deposited are monoclinic, and optically inactive; the mother-liquors from these deposit the crystals with hemihedral faces.

Synthetically prepared racemic acid yields a double sodioammonium salt, which crystallises in monoclinic, optically inactive crystals.

P. P. B.

Mucobromic Acid, $C_4H_2Br_2O_3$. By O. R. Jackson and H. B. Hill (*Deut. Chem. Ges. Ber.*, **11**, 1671—1677).—Pyromucic acid was treated with a slight excess over the calculated quantity of bromine, which was allowed to flow rapidly in, and the mixture kept boiling for a quarter of an hour. The acid was recrystallised from water (m. p. 120—121°). *Barium Mucobromate*, $Br(C_4HBr_2O_3)_2$.—Obtained by well triturating the acid with water and barium carbonate, and heating to 50—60°. The salt washed with ether forms small rhombic plates. Above 100° decomposition sets in, gaseous products, possessing a pungent odour, being liberated. *Silver Mucobromate*, $AgC_4HBr_2O_3$.—On adding silver nitrate to the solution of the calcium salt prepared in the cold, fine interlaced needles separate, soluble in cold water. This salt discolours rapidly when exposed to light, and decomposes at once with alcohol or on warming with water, silver bromide and metallic silver separating. *Ethyl Salt*, $C_2H_5.C_4HBr_2O_3$.—Saturating the alcoholic solution of the acid with hydrochloric acid, and precipitating with water, yields it as a quickly crystallising oily body. This process frequently repeated yields it in white rhombic prisms (m. p. 50—51°). Soluble in alcohol, ether, and chloroform.

Bromo-mucobromic Acid, $C_4HBr_3O_2$.—Obtained by treating mucobromic acid with excess of phosphorus pentabromide at 110—115°, and subsequent treatment with water. At a low temperature it crystallises from alcohol in long white needles (m. p. 53—54°). Very soluble in alcohol, ether, chloroform, benzene, glacial acetic acid, and carbon bisulphide. On dropping it into alkaline solutions, decomposition ensues, accompanied with colour changes passing through blue, green, and orange ; a yellow precipitate is also deposited, and alkaline bromide is formed. The formation of this acid indicates the existence of a hydroxyl group in mucobromic acid, and this fact is further confirmed by the action at 120° of acetyl chloride on mucobromic acid, whereby *acetyl mucobromate*, $C_4HBr_2O_3.C_2H_3O$, is formed. Long needles (m. p. 53—54°), soluble in alcohol, ether, and chloroform.

Barium Dibromacrylate, $Ba(C_3HBr_2O_2)_2$.—By the action of excess of boiling baryta-water on mucobromic acid, malonic acid was obtained (*Ber.*, **11**, 289). By adding mucobromic acid, little by little, to the crystalline mass barium hydrate, obtained by suddenly cooling a hot saturated solution, the above-named salt is formed, and crystallises from dilute alcohol in shining scales, permanent in the air, and over sulphuric acid *in vacuo*. *Silver Dibromacrylate*, $Ag.C_3HBr_2O_2$.—Obtained from the free acid or barium salt. Long needles, crystallisable from hot water. *Lead salt*, $Pb(C_3HBr_2O_2)_2$.—Easily soluble in hot water, with difficulty in cold. Crystallises in broad rhombic plates.

Dibromacrylic Acid, $C_3H_2Br_2O_2$.—Obtained on decomposing the solution of the barium salt with dilute hydrochloric acid, and agitation with ether. On evaporation, the crystalline acid is left in small rhombic prisms (m. p. 83—84°), easily soluble in alcohol, ether, and chloroform, with more difficulty in benzene. In hot water it first

melts to a colourless oil, and then dissolves. On boiling with excess of baryta-water, barium malonate was obtained; it is not improbable from this that the acid is the β-dibromacrylic. The endeavour will be made to obtain β-dichloracrylic acid from mucochloric acid, following Wallach and Hunäns (*Ber.*, **10**, 557 and 2128).

From the solution filtered from the barium dibromacrylate, two acids were obtained; the one was the dibromacrylic acid, melting at 83—84°, the other was in all probability brompropiolic acid, although it could not be isolated in the pure state. The barium salt, $Ba(C_3BrO_2)_2$, was obtained, however. It is easily soluble in water and alcohol, and crystallises in small needles. The endeavour to obtain the acid from this salt was partially successful. A crystalline acid was obtained, which quickly volatilised in the air, and melted between 55° and 65°. Easily soluble in water, alcohol, and ether.

By the action of barium hydrate on mucobromic acid, β-dibromacrylic and formic acids are first produced: $C_4H_2Br_2O_3 + H_2O = {}^*C_3H_2Br_2O_2$; and on boiling the dibromacrylic acid passes partly into *malonic acid*, $C_3H_2Br_2O_2 + 2H_2O = C_3H_4O_4 + 2HBr$, and partly by decomposition into bromacetylene and carbonic anhydride, $C_3H_2Br_2O_2 = C_2HBr + HBr + CO_2$, in all probability with a previous transitory formation of brompropiolic acid, $C_3H_2Br_2O_2 = C_3HBrO_2 + HBr$, which easily splits up into carbonic anhydride and bromacetylene. In absence of more complete knowledge of the nature of the dibromacrylic acid, it is considered that the following formula best explains the decompositions just referred to—

$$CBr_2{=}C{=}C(OH).COOH.$$ W. S.

Methyltaurine, Methyltaurocyamine, and Taurocyamine. By E. Dittrich (*J. pr. Chem.* [2], **18**, 63—78).—*Methyltaurine*, $NH(CH_3).C_2H_4SO_2OH$.—The chloroethylsulphuric chloride prepared by Kolbe's method (*Annalen*, **120**, 33) was converted into the corresponding acid by heating with water, and the silver salt heated in sealed tubes at 110—120° for six hours with concentrated aqueous methylamine solution. The liquid, after being boiled with baryta-water, and the excess of the latter removed with sulphuric acid, yielded methyltaurine on evaporating. A still better method was to heat the methylamine salt of chlorethylsulphuric acid with methylamine solution at 110—120° in a sealed tube. $C_2H_4.Cl.SO_2OH.N(CH_3)H_2 + N(CH_3)H_2 = NH(CH_3).C_2H_4.SO_2OH + N(CH_3)H_3Cl$.

Methyltaurine forms lustrous prisms of the anorthic system, which are anhydrous (m. p. 241—242°). The crystals are soluble in hot and cold water, insoluble in ether and alcohol. The body is seven and a half times more easily soluble in water at 0° than taurine is. Methyltaurine is decomposed by fusion with potash, methylamine being given off. On treatment with nitrous acid, isethionic acid is formed just as with taurine, nitrogen being evolved. The solution has an acid reaction, but the acid character of the body is much weaker than that of taurine. Taurine in alkaline solution is not precipitated by alcohol, whereas methyltaurine is precipitated at once and un-

* *Note by Abstractor.*—Misprinted in text as $C_2H_2Br_2O_2$.

altered. It is soluble in hydrochloric and nitric acids, and crystallises unaltered from these solutions. No double platinum salt could be obtained in the hydrochloric acid solution.

Methyltaurocyamine, $C_2H_4(C_2H_6N_3).SO_2OH$.—Equivalent weights of methyltaurine and cyanamide were dissolved in as little water as possible, and heated for four or five hours at 110—120° in a sealed tube. The reaction—

$$NH(CH_3)C_2H_4.SO_2OH + CNNH_2 = C_2H_4(C_2H_6N_3)SO_2OH$$

then takes place. It is thus proved that methyltaurine unites with cyanamide just in the same manner as glycocol, sarcosine, and methylamidopropionic acid. Strecker's method,—leaving a concentrated aqueous solution of methyltaurine and cyanamide for ten days, until crystallisation sets in,—gave the same yield. Addition of a few drops of ammonia, instead of assisting, seemed to prevent formation of the taurocyamine. It forms large lustrous prisms (monoclinic) with 1 mol. cryst. water, which was lost at 110°. Soluble in cold water with difficulty, with ease in hot; quite insoluble in alcohol and ether. The crystals turn brown at 285° without melting, and on platinum foil diffuse the same odour as methyltaurine. By dissolving methyltaurocyamine in hydrochloric acid, and evaporating with platinum tetrachloride, no double platinum salt could be obtained. Alcohol precipitates from such a mixed solution a white crystalline body resembling methyltaurocyamine; it is, however, possible it may be methyltaurocyamidine.

Taurocyamine, $C_2H_4(CH_4N_3).SO_2OH$.—Equivalent weights of cyanamide and taurine were heated with enough water to dissolve them in a sealed tube for five hours at 110—120°. The body crystallises from water in small white hexagonal prisms (m. p. 224—226°), which are quite insoluble in alcohol and in ether.

The melting points of taurine, methyltaurine, taurocyamine, and methyltaurocyamine are well worthy of note. Taurine melts above the boiling point of mercury; methyltaurine at 241—242°. It would be expected that taurocyamine should fuse with difficulty, and methyltaurocyamine with ease; the opposite, however, is the case. Again, taurine is with difficulty soluble in cold water, methyltaurine with ease. On the contrary, taurocyamine dissolves easily, methyltaurocyamine with difficulty. Taurocyamine dissolves in strong acids. No double platinum salt could be obtained from the solution in hydrochloric acid. W. S.

Allantoxanic Acid. By J. Ponomareff (*Deut. Chem. Ges. Ber.*, **11**, 2156—2157).—This acid is bibasic, forming two series of salts. Both the acid and normal salts are crystalline. The normal salts of the alkalis and alkaline earths are obtained by the action of the bases on the acid salts, and are reconverted into the latter by cold acetic acid. The acid salts are decomposed on boiling with acetic acid, with evolution of carbonic acid. The normal lead salt is precipitated on adding lead acetate to solutions of the acid salts of the alkalis, and is not decomposed by acetic acid. The following salts have been investigated:—

$C_4HN_3O_4K_2.H_2O$; $C_4H_2N_3O_4.NH_4$; $C_4H.N_3O_4.(NH_4)_2$, $(C_4H_2N_3O_4)_2Ba.6H_2O$, $C_4HN_3O_4Ba.2H_2O$; $(C_4H_2N_3O_4)_2Pb.1\frac{1}{2}H_2O$, $C_4H.N_3O_4Pb$; $C_4H_2N_3O_4.Ag$, and $C_4H.N_3O_4Ag_2$.

The acid ethyl salt was obtained as a dense liquid by the action of ethyl iodide on the hydrogen silver salt. It is saponified by potash, yielding the normal potassium salt. It is decomposed when heated with water, with evolution of carbonic anhydride. The acid potassium salt is decomposed on boiling with water into biuret and potassium formate. Salts of allantoic acid are decomposed by mineral acids with evolution of carbonic anhydride and formation of allantoxaidin, $C_3N_3H_3O_2$. The latter compound crystallises from its aqueous solution in small prisms containing 1 mol. H_2O, which it loses on exposure to the air. It is easily soluble in hot water, slightly in alcohol. The aqueous solution has an acid reaction, and decomposes the carbonates of the alkalis and alkaline earths, forming salts. The potassium salt has the composition $C_3N_3H_2O_2K$. Allantoxaidin is decomposed on heating, with evolution of ammonia and cyanic acid. On boiling with acids or water, it is resolved into biuret and formic acid.

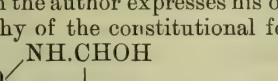
The product of the reduction of potassium allantoxanate by sodium amalgam is the compound $C_8H_{10}N_6O_7$. This acid, which the author terms *hydroxanic*, is precipitated in the form of needles on adding a mineral acid to solution of its soluble salts. It is not decomposed by boiling with nitric or hydrochloric acids (? concentrated), but at 150° is decomposed by the latter into carbonic oxide and anhydride and ammonia.

It is a bibasic acid. The following normal salts have been investigated:—

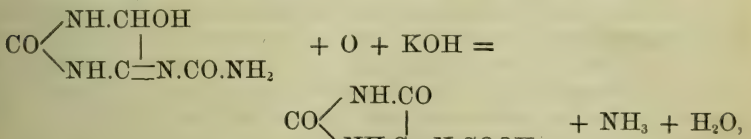
$C_8H_8N_6O_7K_2$, $C_8H_8N_6O_7Na_2$, $C_8H_8N_6O_7(NH_4)_2$, $C_8H_8N_6O_7Mg.4H_2O$, $C_8H_8N_6O_7.Ba.2H_2O$, $C_8H_8N_6O_7.Pb1\frac{1}{2}H_2O$, and $C_8H_8N_6O_7.Ag_2.3H_2C$.

No acid salts could be obtained. Hydroxanic acid is oxidised by boiling aqueous bromine to biuret, with evolution of carbonic oxide and anhydride. By potassium permanganate in alkaline solution it is oxidised to allantoxanic acid.

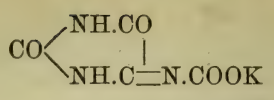
In conclusion the author expresses his opinion that the following is the most trustworthy of the constitutional formulæ hitherto suggested for allantoin:—



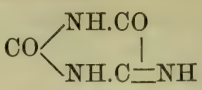
. On this hypothesis its conversion into allantoxanic acid in presence of potassium hydrate is represented by the following equation:—



and the formation and constitution of allantoxaidin by the following:—



$$+ HCl = KCl + CO_2 +$$



C. F. C.

Some Derivatives of Allantoïn. By G. Ponomareff (*Deut. Chem. Ges. Ber.*, **11**, 2155—2156).—Allantoïn when dissolved in potash solution is slowly converted into allantoic acid, which is separated in microscopic needles on the addition of sulphuric acid. This acid, when boiled with water, is resolved into urea and allanturic acid, $C_3N_2H_4O_3$. The latter is identical with the product of the similar decomposition of uroxanic acid (*Ber.*, **9**, 1162). Allantoic acid forms crystalline salts with the alkalis and alkaline earths, which are not decomposed by acetic acid. The following have been investigated :—

$C_4H_7N_4O_4Na.H_2O$; $C_4H_7N_4O_4(NH_4)$; $(C_4H_7N_4O_4)_2Ba.2H_2O$,

and in addition $(C_4H_7N_4O_4)_2Pb.H_2O$ and $C_4H_7N_4O_4Ag$. C. F. C.

Hydrocarbons obtained by the Action of Aluminium Chloride on Methyl Chloride and Benzene. By E. Ador and A. Rilliet (*Deut. Chem. Ges. Ber.*, **11**, 1627—1630).—According to the method of Friedel and Crafts, methyl chloride was passed into toluene containing 15 to 20 per cent. of aluminium chloride. The pure hydrochloric acid which is given off was allowed to escape through a mercurial column 5—6 cm. high. On boiling the product with sodium, and fractionating, two fractions were obtained, one boiling at 138—141°, and the other at 135—140°. Both fractions yielded terephthalic and isophthalic acids when treated with oxidising agents. In proportion to the isophthalic acid formed, the quantity of terephthalic acid is very small, and the authors consider that in the original mixture, now seen to be that of iso- and para-xylene, the proportion of para-xylene could not be more than 5 per cent. at most. No orthoxylene could be detected. The results show that these synthetic xylenes contain very little orthoxylene, but that isoxylene is almost exclusively formed, together with a little paraxylene. W. S.

Constitution of the Propyl Group in Cymene. By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **11**, 1049—1052).—The constitution of the propyl group of cymene remaining, notwithstanding the researches of Fittig and Fittica, to a certain extent an open question, the author has prepared a number of derivatives of the synthetical hydrocarbon (from parabromtoluene and normal propyl iodide) for the purpose of comparison with similar characteristic derivatives of camphor cymene. Complete identity was thus established in the case of the sulphonic acid (*i.e.*, barium salt as to crystallisation, composition, and solubility, and sodium salt) and the sulphamide, together with its silver compound, proving, therefore, the identity of the hydrocarbons.

The attempt to extend the comparison to the derivatives of the isomeride containing the isopropyl group was unsuccessful, from the failure to synthesise this body. C. F. C.

Mode of Action of Sulphuric Hydroxychloride. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, **11**, 2061—2066).—The action of sulphuric hydroxychloride on hydrocarbons may be represented, *à priori*, by three equations:—

$$(a.)\ SO_2Cl.OH + RH = SO_2R.OH + HCl.$$
$$(b.)\ SO_2Cl.OH + RH = SO_2ClR + H_2O.$$
$$(c.)\ SO_2Cl.OH + 2RH = SO_2R_2 + HCl + H_2O.$$

The authors have investigated the decomposition of certain hydrocarbons by this reagent, in order to ascertain which of these is therein realised.

1. *Toluene.*—1 mol. by 1 mol. sulphuric chloride. The products of the reaction were sulphotoluide, paratoluene-sulphochloride, and paratoluene-sulphonic acid, the latter occurring in largest quantity. Since sulphotoluide results from the reaction of 1 mol. sulphuric hydroxychloride and 2 mols. toluene, the presence of some quantity of undecomposed sulphuric chloride also observed in the product of the reaction is accounted for. Toluene-sulphonic acid being the chief product, the essential reaction would appear to be that indicated by (*a*); at the same time the formation of this body may be explained as resulting from the decomposition of toluene-sulphonic chloride by water, indirectly, therefore, according to equation (*b*). The proof that such is actually the case is afforded by a second experiment, in which the reaction was allowed to proceed in presence of phosphoric anhydride; the quantity of the sulphonic chloride was thereby much increased. The authors therefore conclude that in the case of toluene the decompositions represented by *a* and *b* both occur, and to a like extent; that indicated by *c* occurring also, but only to a very limited extent.

2. *Xylene.*—1 mol. isoxylene by 1 mol. sulphuric hydroxychloride. The chief product was a xylene-sulphonic acid (m. p. 137°), identical with that described by Jacobsen (*Ber.*, **10**, 1014) as "erste metaxylolsulfonsäure." A small quantity of the chloranhydride of this acid was also obtained.

3. *Monochlorobenzene.*—1 mol. by 1 mol. chlorosulphonic acid. The chief product was a chlorobenzene-sulphonic acid, which, from the melting point of its chloride (55°) and of the corresponding amide (142°) proved identical with that discovered by Hutchings (*Jahresber.*, 1857, 450). In addition there was formed a dichloro-sulphobenzide, $(C_6H_4Cl)_2SO_2$, apparently identical with that obtained by Otto (*Annalen*, **145**, 28) by the action of SO_3 upon C_6H_5Cl.

4. *Monobromobenzene.*—1 mol. by 1 mol. sulphuric hydroxychloride. A dibromo-sulphobenzide was formed in some quantity, 16 grams of bromobenzene yielding 6 grams of this product. It crystallised from alcohol in long needles, melting at 172°, and boiling undecomposed at a higher temperature. A bromobenzene-sulphonic acid was also obtained, which, from the investigation of its chloride and amide, was found to be identical with that of the para-series obtained by Couper (*Annalen*, **104**, 226) by dissolving bromobenzene in fuming sulphuric acid.

5. *Thiophenol.*—Orlowsky having, by the reaction of phenol (2 mols.)

with sulphuric hydroxychloride (1 mol.), obtained the true phenol ether of sulphuric acid, thiophenol might be expected to react similarly to form the corresponding thio-ether. Such is not the case, however. There are formed phenyl disulphide, sulphurous anhydride, hydrochloric acid, and water, according to the equation $2C_6H_5.SH + SO_2Cl.OH = (C_6H_5)_2S_2 + SO_2 + H_2O + HCl$.

6. *Paratoluene Sulphydrate.*—2 mols. by 1 mol. sulphuric hydroxychloride. The reaction closely resembles the preceding. Paratoluene disulphide (m. p. 43°) is formed, together with sulphurous anhydride and hydrochloric acid. C. F. C.

β-Chlorcymene from Thymol. By E. v. Gerichten (*Deut. Chem. Ges. Ber.*, **11**, 1719—1722).—To determine the exact nature of the acid resulting from the oxidation of β-chlorcymene, the formula for which may be either $C_6H_3(CH_3)Cl.C_2H_4.COOH$ or $C_6H_3(C_3H_7)Cl.COOH$, the author prepared bromocymene by acting on thymol with phosphorus pentabromide. The product of this reaction, boiling at 224—226°, yielded, on oxidation, an acid whose barium salt crystallises in leaflets having a pearly lustre resembling that of the chloro acid, but the quantity obtained was insufficient for further study. In the hope of identifying this acid with bromocumic acid, some of the latter was prepared from cumic acid by the direct action of bromine. The acid so obtained melts at 151—152°, and forms a barium salt crystallising in beautiful plates. It is identical with that described by Naquet and Louguinine (*Jahresber.*, 1866, 371).

The acid obtained from β-chlorcymene yields, when treated with sodium amalgam, an acid crystallising in long white needles (m. p. 103°). This latter acid is insoluble in cold, but soluble in hot water, alcohol, and ether. Analyses of its silver salt show its composition to be $C_6H_4(CH_3).C_2H_4.COOH$. Between the melting point of this acid and that of paratoluic acid there is a difference of 74°. The same difference exists between the melting points of benzoic and hydrocinnamic acid. From this the author infers that the acid is paramethylhydrocinnamic acid.

In concluding, the author shows that in β-chlorcymene the chlorine atom does not completely prevent the oxidation of the neighbouring side chains, and contends that Remsen is not sufficiently justified in using the fact that negative elements prevent the oxidation of their neighbouring side chains, as a principle by which to determine the constitution of such compounds as bromparaethyltoluene and others.

P. P. B.

Action of Hydrogen Sulphide on Certain Nitro-compounds. By F. Beilstein and A. Kurbatow (*Deut. Chem. Ges. Ber.*, **11**, 2056—2057).—1. *Chlorodinitrobenzene*, (m. p. 50°), yields, on treatment with alcoholic ammonium sulphide, potassium sulphide or sulphydrate, and *m*-dinitrophenyl sulphide $\{C_6H_3,(NO_2)_2\}_2.S$. This body crystallises from glacial acetic acid in yellow needles (m. p. 193°); it is almost insoluble in alcohol and benzene. By oxidation with nitric acid (sp. gr. 1·5) at 120°, it is converted, although with difficulty, into the sulphone, $\{C_6H_3.(NO_2)_2\}_2SO_2$, crystallising from nitric acid in yellowish prisms

(m. p. 240°), which are very slightly soluble in alcohol and carbon bisulphide.

2. *Nitro-paradichlorobenzene*, $C_6H_3Cl(NO_2)Cl = [1:2:4]$, (m. p. 54·5°), is converted by alcoholic potassium sulphide into chlornitrophenyl sulphide $\{C_6H_3Cl(NO_2)\}_2S$, crystallising from acetic acid in dark yellow needles (m. p. 150°), almost insoluble in alcohol; by alcoholic potassium sulphydrate into chlornitrothiophenol, $C_6H_3Cl(NO_2).SH$, crystallising from glacial acetic acid in yellow plates (m. p. 212°). By the further action of ammonium sulphide on this body it is converted into a complex thio-compound, $C_{12}H_8Cl_2N_2S_3$ according to the equation, $2C_6H_3Cl(NO_2).SH + 4H_2S = C_{12}H_8Cl_2N_2S_3 + 3S + 4N_2O$. This product crystallises from glacial acetic acid in yellow needles (m. p. 147°). It is a weak base; its constitution is probably

$$\begin{matrix} C_6H_3Cl.(SH)N \\ \qquad\qquad \diagdown S. \\ C_6H_3Cl.(SH)N \end{matrix}$$

It is rapidly oxidised by nitric acid (sp. gr. 1·34) to $C_6H_3ClN_2S$; this body volatilises from its boiling aqueous solution. By recrystallisation from aqueous alcohol, it is obtained in large colourless needles (m. p. 103·5°) which are easily soluble in alcohol and in carbon bisulphide. It is very stable; its constitution is probably that represented by the formula $C_6H_3Cl\begin{matrix} N \\ \diagup\!\diagdown \\ S \end{matrix}\!\!>N$.

3. *Chlor-orthodinitrobenzene*, $C_6H_3Cl(NO_2)(NO_2) = [1:3:4]$ (m. p. 38°) is converted by alcoholic potassium sulphydrate into *chloronitrothiophenol*, $C_6H_3Cl(SH)(NO_2) = [1:3:4]$, crystallising from acetic acid in yellow needles (m. p. 171°) easily soluble in benzene and in carbon bisulphide.

4. *Nitro-metadichlorobenzene*, $C_6H_3Cl(NO_2)Cl = [1:3:5]$ is rapidly attacked by the alcoholic sulphydrate, tetrachlorazoxybenzide, $(C_6H_2Cl_2)_2N_2O$, is formed and separated, symmetrical dichloraniline remaining in solution. The former compound the authors find to melt at 171—172°, the latter at 51—52°, boiling at 260°.

From these and other observations on the chlornitro-derivatives, the authors conclude that they are reduced by hydrogen sulphide only at those points where the nitro-group is not in immediate proximity to a chlorine atom or second nitro-group. C. F. C.

Compounds of Organic Bases with Mercuric Chloride. By O. Klein (*Deut. Chem. Ges. Ber.*, **11**, 1741—1744).—When an alcoholic solution of 4 mols. of dimethylaniline is mixed with an aqueous solution of 3 mols. of mercuric chloride, the following reaction takes place: $3HgCl_2 + 4C_6H_5N(CH_3)_2. + H_2O = Hg_2OCl_2[C_6H_5N(CH_3)_2]_2 + HgCl_2 + 2C_6H_5N(CH_3)_2 + 2HCl$. The basic compound,

$$Hg_2OCl_2[C_6H_5N(CH_3)_2]_2,$$

separates out at once in the form of white needles; it is almost insoluble in hot water, and only sparingly soluble in alcohol and in ether. Hot benzene dissolves it easily and deposits it on cooling in plates having a

mother-of-pearl lustre. Hydrochloric acid converts this compound into the soluble double salt formed in the above reaction; ammonia precipitates it from the solution, but it dissolves in an excess of ammonia; from the ammoniacal solution, it is partly precipitated by hydrochloric acid. It becomes blue on exposure to light, more easily when heated. On heating it to 100° a blue colouring matter is formed, which is soluble in alcohol, but insoluble in water; hydrochloric acid dissolves this colouring matter, forming a yellow solution which, when diluted with water, changes to green and finally blue. Ammonia also colours the hydrochloric acid solution blue. The blue alcoholic solution is decolorised by nascent hydrogen.

The double salt, $HgCl_2 + 2C_6H_5N(CH_3)_2HCl$, the second product of the above reaction, crystallises from water in well formed thick plates. By slow evaporation of the aqueous solution, it may be obtained in compact prismatic forms with pyramidal faces. Cold water and alcohol dissolve it sparingly, but it is easily soluble in these solvents when hot. Ether and benzene dissolve it sparingly. It is not changed by exposure to air, and melts at 149°. Part only of this salt separates out from the filtrate of the basic compound; if the filtrate is concentrated and more $HgCl_2$ added, then a thick oil is obtained, which becomes crystalline if cooled and a crystal of the double compound added. P. P. B.

Experimental Determinations of Position. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **11**, 1650—1652).—A method has been given to distinguish the orthodiamines from their isomerides. The diamine hydrochloride is simply heated at 100° with benzaldehyde, and it is noticed if hydrochloric acid gas be evolved or not. If so, the body is an orthodiamine. The method has been first well tested, and finally employed to the determination of two, as yet, uncertain diamines, and in order to throw light upon the constitution of a third, the α-naphthalenediamine.

α and β-Naphthalenediamine.—α-Nitronaphthalene treated with nitric acid gave two isomeric dinitronaphthalenes, α and β, melting at 215° and 170° respectively, according to Darmstädter and Wichelhaus (*Ber.*, **1**, 274). The latter melting at 170°, is now found to be the α-β-dinitro-derivative. The separation was effected (*Ber.*, **5**, 370) by means of glacial acetic acid and benzene, the reduction with stannous chloride in alcoholic solution with hydrochloric acid. The α-naphthalene-diamine was found not to be an ortho-compound, but it may possibly be a para-compound, since it is formed at the same time as β-dinitronaphthalene, an ortho-compound. The hydrochloride of the diamine obtained from the β-dinitronaphthalene, was heated at 100° until all hydrochloric acid ceased to be given off, and then was again heated to 100° with a little benzaldehyde. There was a considerable evolution of hydrochloric acid gas, and the body is therefore an ortho-diamine-hydrochloride. This diamine melting at 170° may therefore be regarded as the α-β-diamine.

Ortho-metatoluylene-diamine.—This body was prepared from orthotoluidine by Beilstein and Kuhlberg's method (*Annalen*, **158**, 335). On applying the test above mentioned, only a minute evolution of

hydrochloric acid gas was observed, indicating that the ortho-compound was probably contained to a small extent only in the preparation. That this was a mixture was proved by testing the mother-liquors of the nitrotoluidine melting at 129°—130·5°, which yielded crystals melting at 122°. After reduction, the difficultly soluble tin double salt was isolated, and the hydrochloride from it did not give a trace of hydrochloric acid with benzaldehyde. The hydrochloride obtained from the mother-liquors of this tin salt, however, gave on heating with benzaldehyde a very considerable evolution. It follows that this so-called ortho-diamine obtained from the orthotoluidine, chiefly consists of the [1 : 2 : 5] body (CH_3 at 1), for the nitrotoluidine melting at 130° and belonging to it, furnishes meta-nitrotoluene by the action of nitrous acid and alcohol. The body present in small quantity might possibly be [1 : 3 : 4] tolylene-diamine (from paratoluidine) mixed with some of the ortho-toluidines. W. S.

Simple Method for Preparing Aldehydines. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **11**, 1648—1650).—By agitating dilute aqueous solutions of an ortho-diamine hydrochloride with an aldehyde, the aldehydine is formed, the action being accompanied by rise of temperature. Thick masses are formed, which after some time, or on addition of a little alcohol and shaking, quickly pass into the colourless crystalline hydrochloride of the new base, which requires several recrystallisations before it is quite pure. The yield is 50—70 per cent. of the theoretical.

Five parts by weight of ortho-toluylene-diamine hydrochlorides were dissolved in 100 parts of water and skaken with 5 parts of benzaldehyde, whereby a thick mass was obtained, which on standing 12 hours changed into a white crystalline salt. This was filtered, washed with ether, pressed, dissolved in hot water with addition of some hydrochloric acid. The precipitate was recrystallised from hot very dilute hydrochloric acid, forming white needles consisting of pure tolubenzaldehydine hydrochloride. The yield was 62 per cent. of the theoretical. (The preparation of furfur-aldehydine was even more successful). $C_6H_4(NH_2HCl)_2 + 2C_7H_6O = C_6H_4(N.C_7H_6)_2.HCl + 2H_2O + HCl$. It is not improbable that this reaction, which proceeds at ordinary temperatures and in aqueous solution, may play a part in the vegetable economy, and contribute to the formation of the so-called alkaloïds. W. S.

The Aldehydines. By A. Ladenburg and L. Rügheimer (*Deut. Chem. Ges. Ber.*, **11**, 1656—1661).—1. *Dibenzylidene-amidobenzoic acid*, $C_{21}H_{16}N_2O_2$, obtained by oxidising tolubenzaldehydine with potassium permanganate. This acid resists the action of concentrated hydrochloric acid at 200°, separating out in large crystals, which form a grey tough mass on heating at 220° for several hours. In the oxidation of the tolubenzaldehydines, the CH_3 group is simply changed to a COOH group, and the following formula is assigned to the product :—

$$COOH.C_6H_4{<}\begin{matrix}N{=}C_7H_6\\ N{=}C_7H_6\end{matrix}.$$

Calcium salt, $(C_{21}K_{15}N_2O_2)_2Ca$. Obtained by dissolving the acid in excess of potassium carbonate, and treating with calcium chloride, and afterwards filtering and allowing to crystallise. Needles or six-sided prisms, soluble in alcohol, with difficulty in cold water, but more easily in hot. *Silver salt*, $C_{21}H_{15}N_2O_2Ag$, a floccular precipitate.

2. *Tolufurfur-aldehydine*, $C_{17}H_{14}N_2O_2$, prepared by treating an aqueous solution of ortho-tolylene-diamine hydrochloride with furfural, whereby the crystalline hydrochloride of the base is obtained. This was dissolved in very dilute hydrochloric acid, and after decolorising the solution with animal charcoal, the base was precipitated by potash and recrystallised from petroleum spirit. It melts at 128·5°. *Methiodide*, $C_{17}H_{14}N_2O_2.CH_3I$. Obtained by warming the base with methyl iodide at 100°, and crystallising twice from hot water. Beautiful shining scales, melting at 195·5°, decomposing, and forming a dark fluid. Soluble with difficulty in cold water and in alcohol, and has an extremely bitter taste, nearly equal to that of strychnine. It is a strong poison. Its chloride has been prepared. The *methochloride*, $C_{17}H_{14}N_2O_2.CH_3Cl$, forms colourless shining scales, easily soluble in water. It is a powerful poison, producing stupefaction and paralysis on injection. *Platinum salt*,* $(C_{17}H_{14}N_2O_2.CH_3Cl)_2.PtCl_4$. The *tri-iodide*, $C_{18}H_{17}N_2O_2I_3$, obtained in light brown needles (m. p. 126—128°) by treating the alcoholic solution of the methyl-iodide compound with a proportionately small quantity of alcoholic iodine solution, and recrystallising from alcohol. The *penta-iodide*, $C_{18}H_{17}N_2O_2I_5$, is obtained by treating the mother-liquor from the last compound, with excess of iodine solution, whereby a brown-black precipitate is formed. On crystallising from alcohol, dark steel-blue prisms separate (m. p. 109°).

3. *Phenylanis-aldehydine*, $C_{22}H_{20}N_2O_2$, prepared from anis-aldehyde, and a dilute aqueous solution of ortho-phenylene-diamine hydrochloride, with addition of a little alcohol. The base was separated from the hydrochloride by ammonia, and recrystallised from alcohol repeatedly. Stellate needles, (m. p. 128·5—129°), very soluble in hot alcohol. The hydrochloride forms needles almost insoluble in water.

4. *Tolu-anis-aldehydine*, prepared like the preceding, crystallises in needles, easily soluble in alcohol and chloroform, with difficulty in petroleum spirit (m. p. 152—156°). W. S.

Some Phenyl-aldehydines. By A. Ladenburg and T. Engelbrecht. 1. *Phenyl-benzaldehydine*, $C_6H_4(NC_7H_6)_2$, colourless six-sided prisms, insoluble in water, nearly so in alkaline hydrates, but easily in alcohol and benzene (m. p. 133—134°). Prepared by agitating a

* *Note by Abstractor.*—This formula is given in the text as follows :—

$$(C_{18}H_{17}N_2O_2.HCl)_2.PtCl_4,$$

but this appears to be incorrect, containing 1 H too much, thus—

$$\underbrace{(C_{17}H_{14}N_2O_2(H)}_{\text{The base.}}.\underbrace{CH_3Cl)_2}_{\text{Methyl chloride.}}.PtCl_4.$$

dilute aqueous solution of ortho-phenylene-diamine with benzaldehyde. The crystalline mass forming after some time, is recrystallised from very dilute hydrochloric acid, and this crystalline hydrochloride is decomposed by potash. Like other aldehydines, it is mono-acid. *Phenyl-benzaldehydine hydrochloride*, $C_{20}H_{16}N_2.HCl$, prepared as above mentioned, forms colourless prisms, difficultly soluble in water, and decomposed on boiling, with separation of hydrochloric acid. No crystalline water. *Platinum double salt*, $(C_{20}H_{16}N_2.HCl)_2PtCl_4$, crystallises from dilute alcohol, with addition of hydrochloric acid, in golden-yellow needles. The *nitrate*, $C_{20}H_{16}N_2.HNO_3$*, colourless prisms, slightly soluble in cold water. *Sulphate*, $C_{20}H_{16}N_2.H_2SO_4$. Phenyl-benzaldehydine is dissolved in hot dilute sulphuric acid, and on cooling the salt crystallises out. On recrystallising, small, colourless, shining plates are obtained. *Ethiodide*, $C_{20}H_{21}N_2.P_2H_5I$.—The base heated at 100°—120° in sealed tubes for some hours with ethyl iodide, yields the ethiodide, crystallising from water in well-formed crystals (m. p. 211—213°). The *methiodide*, $C_{20}H_{16}N_2.CH_3I$, obtained like the eth-iodide, forms shining prisms.

2. *Phenylfurfur-aldehydine*, $C_6H_4(NC_5H_4O)_2$, prepared like the phenylbenzaldehydine, substituting furfurol for benzaldehyde. On recrystallisation from heavy petroleum spirit, it was obtained in colourless crystals—

$$C_6H_4(NH_2)_2 2HCl + 2C_5H_4O_2 = C_6H_4N_2(C_5H_4O)_2HCl + 2H_2O + HCl.$$

The base is mono-acid (m. p. 95—96°), easily soluble in alcohol, less so in benzene, still less in petroleum spirit, insoluble in water. It dissolves easily in hydrochloric acid, forming the hydrochloride, the crystals of which appear to decompose on washing. The *platinum salt*, $(C_{16}H_{12}N_2O_2.HCl)_2PtCl_4$, was obtained in the pure state by adding platinic chloride to the hydrochloric acid solution of the chloride. It forms yellow plates. The *nitrate*, $C_{16}H_{12}N_2O_2.HNO_3$.: this salt, prepared by addition of dilute nitric acid to dilute solutions of the hydrochloride, is very characteristic for this base, as also for the homologous tolufurfuraldehydine. It crystallises in needles. The *sulphate*, $C_{16}H_{12}N_2O_2.H_2SO_4$. Only the acid sulphate could be obtained, just as with the preceding base. The ethyl and methyl iodides, and the ethyl chloride platinum salt were also prepared. W. S.

The Three Isomeric Tolidines (Diamido-ditolyls). By A. Goldschmidt (*Deut. Chem. Ges. Ber.*, **11**, 1624—1626).—Petrieff obtained a tolidine from hydrazo-toluene, derived from ortho-nitrotoluene (*Ber.*, **6**, 557), and Werigo obtained the azo-derivatives of para-nitrotoluene (*Zeits. Chem.* 1864, 481, 722; 1865, 631; 1866, 196). From the para-hydrazo-toluene the second tolidine was prepared (*Ber.*, **3**, 549, and **6**, 558). The author modifies the preceding processes advantageously by dissolving the hydrazo-compounds in alcohol and converting them into the tolidine sulphates by addition of dilute sulphuric acid. From the sulphates, ammonia liberates the bases.

* It is stated in the paper that this nitrate is obtained by the addition of *dilute hydrochloric acid* to the solution of the hydrochloride. The words *dilute nitric acid* should probably be substituted for *dilute hydrochloric acid*.—W. S.

These tolidines are distinguished from the hydrazo-compounds by their formation of salts, and by the blue colour reaction they produce on oxidation, by means of bromine-water, ferric chloride, &c. (analogously to benzidine). For the first step in the preparation of the third tolidine, metanitro-para-toluidine was dissolved in alcohol, and nitrogen trioxide passed through the solution until on cooling no further separation of crystals took place. A 60 per cent. yield is thus obtained of the meta-nitro-toluene.

Meta-azotoluene, $C_7H_7N.NC_7H_7$, obtained by boiling meta-nitro-toluene with alcoholic potash. Large red plates (m. p. 51°). It is insoluble in water, but soluble in benzene, alcohol and ether.

Meta-hydrazo-toluene, $C_7H_7NH.HNC_7H_7$. Hydrogen sulphide was passed through the alcoholic ammonia solution of the azo-compound, and on boiling, filtering, and evaporating, the hydrazo-compound crystallised out. Unstable in the air, passing into the azo-compound rapidly.

Tolidine sulphate, $(C_7H_6.NH_2)_2H_2SO_4$, obtained from the hydrazo-compound by addition of dilute sulphuric acid. Beautiful shining plates, easily soluble in water, but insoluble in alcohol.

Tolidine or *diamidoditolyl*, $(C_7H_6.NH_2)_2$. On adding ammonia to the aqueous solution of the sulphate, the base separates in oily drops. Obtained from ether solution in the solid state, with very low melting point. It forms salts with hydrochloric and nitric acids. Ferric chloride produces a blue colour with it.

The three isomeric hydrazo-toluenes thus, therefore, equally allow of the tolidine formation. W. S.

Certain Colouring Matters of the Rosaniline Group. By E. Fischer and O. Fisher (*Deut. Chem. Ges. Ber.*, **11**, 2095—2099).—In a previous communication (*Ber.*, **11**, 951) the authors described a base, formed by the action of chloral and zinc chloride on dimethylaniline in the cold, which they regard as a normal condensation product of the formula, $[C_6H_4.N(CH_3)_2]_3C.CH[C_6H_4.N(CH_3)_2]_2$. They now state that by the action of chloral (1 mol.) upon dimethylaniline (3 mols.) in presence of zinc chloride, added gradually at the temperature of the water-bath, a colourless base is obtained, crystallising in small prisms (m. p. 250°). This body is converted, by oxidation with manganese dioxide and sulphuric acid, into methyl violet, which is thus obtained pure and in theoretical quantity, with simultaneous formation of formic aldehyde. Methyl violet being a pentamethyl derivative of pararosaniline, the base in question appears to be a hexmethylated triamidotriphenylmethane, and its constitution and oxidation may be represented as follows:—

$$[(CH_3)_2.N.C_6H_4]_2CH.C_6H_4.N(CH_3)_2 + O_2 =$$
$$[(CH_3)_2N.C_6H_4]_2C\begin{cases} C_6H_4 \\ | \\ N(CH_3) \end{cases} + H_2O + CH_2O.$$

The oxidation of tetramethyldiamidotriphenylmethane, to form malachite green, and formic aldehyde is, by inference, that represented by the similar equation:—

$$(CH_3)_2N.C_6H_4(C_6H_5)CH.C_6H_4.N(CH_3)_2 + O_2 =$$
$$(CH_3)_2N.C_6H_4(C_6H_5)C\begin{cases} C_6H_4 \\ | \\ N(CH_3) \end{cases} + H_2O + CH_2O.$$

This is additional proof, beyond the observed difference of melting points, that the base obtained by Doebner by reduction from malachite green, is not *tetra-* but *tri*-methyldiamidotriphenylmethane (*Annalen*, **194**, 296, and *Ber.*, **11**, 1240).

The above mode of formation of methyl violet confirms the author's view of the complicated reaction by which it is obtained from dimethylaniline, viz., the methyl groups being detached from a portion, are oxidised to formic acid or aldehyde, which then unites with three other molecules of dimethylaniline, to form hexmethyltriamidotriphenylmethane, and this body, losing one methyl group under further oxidation, is converted into methyl violet. Direct observation shows, in fact, that dimethylaniline yields on oxidation with manganese dioxide and sulphuric acid at 30—40° violet colouring matters, together with formic aldehyde. C. F. C.

Azo-derivatives of Toluene. By Barsylowsky (*Deut. Chem. Ges. Ber.*, **11**, 2153—2155).—The author has further investigated the azo-compound (m. p. 244—245°) which he obtained by the oxidation of paratoluidine (*Ber.*, **6**, 1209, and **8**, 695). The action of chlorine and bromine on this body, although studied under a variety of conditions, yielded no definite results. Of the corresponding hydrazo-body, the compounds with sulphuric, hydrochloric, and nitric acids were obtained in the crystalline state; those with the organic acids are more stable, the oxalate, $(C_{14}H_{16}N_2)_2C_2H_2O_4.H_2O$ being especially characteristic; it is easily soluble in alcohol, slightly in water. The hydrazo-compound yields no definite compounds when heated with ethyl iodide; it reacts with acetic chloride to form the crystalline compound—

$$C_{14}H_{14}N_2(C_2H_3O)_2.$$

In all respects therefore the azo-compound in question differs from the three isomeric azotoluenes; the hydrogen which is in union with nitrogen in this body, being moreover replaceable by acid radicles, this compound is regarded by the author as a polymeride of para-azotoluene, probably $C_7H_7N{=}NC_7H_6.C_7H_6N{=}NC_7H_7$.

The author has also further investigated the meta-azotoluene previously described by him (*Ber.*, **10**, 2097). The corresponding hydrazo-compound is not crystalline; it is converted by the action of acids into a tolidine, which is liquid at ordinary temperatures.

C. F. C.

Metanitrophenol and its Derivatives. By A. Bantlin (*Deut. Chem. Ges. Ber.*, **11**, 2099—2107).—*Metanitrophenol* is formed from metanitraniline by means of the diazo reaction. It is easily soluble in alcohol and ether, crystallises from carbon bisulphide in feathery plates (m. p. 96°), and distils unchanged at 194° under a pressure of 70 mm. It decomposes carbonates, forming beautiful salts; the

potassium salt crystallises with 2 mol. H_2O, in orange-coloured flat needles.

Metanitranisol is obtained from the latter salt by heating it in alcoholic solution with excess of methyl iodide. It crystallises from alcohol in colourless needles, melts at 38°, boils undecomposed at 254°, and is easily volatilised by steam.

Metanitrophenetol, prepared similarly to the preceding, melts at 34°, boils with slight decomposition at 264° under ordinary pressure, and at 169° under a pressure of 70 mm.

Resorcin is easily obtained from metanitrophenol through the amido-compound and diazo reaction.

Trinitroresorcin or *styphnic acid* is formed in theoretical quantity by the long-continued action of boiling concentrated nitric acid on the nitrophenol.

Dinitrophenols.—Three of these compounds are obtained by the action of nitric acid (sp. gr. 1·3) on metanitrophenol. They are separated by taking advantage of the difference of solubilities of their Ba salts in water (δ from γ and ϵ), and alcohol (γ from ϵ).

γ-Dinitrophenol is soluble in ether and in hot alcohol; is easily volatilised by steam, separating on condensation in yellow needles (m. p. 104°). The potassium salt crystallises with 2 mol. H_2O in thick, bright red needles; the barium salt, with 3 mol. H_2O, in slender brown needles; with 2 mol. H_2O, in bright red needles.

δ-Dinitrophenol crystallises from water in long colourless silky needles, which melt under water at 50—60°, in the dry state at 134°. The potassium salt crystallises from water in red needles; the barium salt with 3 mol. H_2O in red-brown prisms.

ϵ-Dinitrophenol crystallises from water in small yellow needles (m. p. 144°). The potassium salt crystallises with 2 mol. H_2O in yellow needles; the barium salt crystallises anhydrous in large brown needles.

Dinitroanisols are obtained by heating the potassium salts of the corresponding nitrophenols with alcohol and methyl iodide at 100°, and also by the action of concentrated nitric acid on metanitroanisol.

γ-Dinitroanisol crystallises from alcohol in bright yellow needles (m. p. 96°); it boils undecomposed above 360°, and is easily volatilised by steam.

δ-Dinitroanisol crystallises in slender golden-yellow needles (m. p. 70°); it is less easily volatilised by steam than the γ-compound.

ϵ-Dinitroanisol crystallises from alcohol in colourless thick plates (m. p. 118°).

Trinitroresorcin was obtained by the action of boiling concentrated nitric acid on the dinitrophenols.

The decomposition of the dinitroanisols by ammonia (alcoholic) is not uniform, the γ-compound being converted into a dinitroaniline, and this by the action of nitrous acid into metadinitrobenzene; δ-dinitroanisol yielded, on the other hand, a nitroanisidine (m. p. 129°), which was converted by the nitrous acid into paranitroanisol (m. p. 52°), and similarly ϵ-dinitroanisol gave a nitranisidine (m. p. 76°) converted by nitrous acid into metanitranisol. The constitution of these bodies is not yet elucidated.

The formation of trinitroresorcin from metanitrophenol must be preceded by that of a tetranitrophenol, one NO_2 group in which is replaced by OH to form styphnic acid. Its probable constitution is represented as $OH : (NO_2)_3 : OH = [1 : 2 : 3 : 4 : 5]$.

The author is further investigating these questions. C. F. C.

Bromonitro- and Bromamido-anisol. By W. Staedel and G. Damm (*Deut. Chem. Ges. Ber.*, **11**, 1749—1751).—*Dibromorthonitrophenol*, $C_6H_2(OH)(NO_2)Br_2 = [1 : 2 : 4 : 6]$, is converted into the methyl ether according to Körner's method, and the ether so formed reduced by tin and hydrochloric acid. The hydrochloride of the dibromorthanisidine so formed crystallises from alcohol or dilute hydrochloric acid in the form of leaflets or needles. The free base is a thick oil solidifying on cooling, its salts may be formed by adding acids to its alcoholic solution. It is a monacid base; the hydrochloride, sulphate, nitrate, and oxalate have been prepared. The sulphate melts at 177° with partial decomposition; the oxalate at 147—148°, decomposition taking place simultaneously with formation of a crystalline sublimate.

Monobromorthonitranisol, $C_6H_3Br(NO_2).OCH_3$, is formed by acting on the silver salt of the corresponding phenol (m. p. 88°) with methyl-iodide. This anisol crystallises from ether in beautiful, slightly yellow, long and wide prisms; it melts at 88°. The constitution of this body is doubtful. By reduction with tin and hydrochloric acid, the corresponding bromorthanisidine is obtained, which crystallises from ether, alcohol, or benzene in beautiful prismatic crystals, melting at 97—98°. By crystallisation from acidified water, the hydrochloride of this monacid base may be obtained in white needles. By heating the alcoholic solution of the base with different acids, the salts may be prepared. The sulphate and the nitrate have been obtained as white crystalline precipitates.

Dibromparanitranisol, $C_6H_2(OCH_3)Br(NO_2)Br = [1 : 2 : 4 : 6]$, may be easily reduced, the base so obtained is under investigation.

P. P. B.

Quercite. By L. Prunier (*Ann. Chim. Phys.* [5], **15**, 5—91).—Braconnot, in 1849, found in acorns a crystalline sugar, not susceptible of fermentation by yeast, which he regarded as lactose.

Dessaignes, in 1851, made a more complete examination of the substance and determined its composition, which he found to be that of mannite *minus* the elements of water. He proposed for it the name of *quercite*.

Berthelot, in 1855, showed that quercite is a polyatomic alcohol, and described several of its compound ethers.

Senarmont, in 1857, determined the crystalline form of quercite, showing that it belongs to the clinorhombic system.

Afterwards little more was done until the subject was taken up by the author. The present paper describes the preparation and properties of quercite, its compounds with acetic, butyric, and hydrochloric acids, and its behaviour with hydrobromic and hydriodic acids.

Preparation and Properties.—The author prepares quercite as follows:—(1.) Decorticated and coarsely powdered acorns are exhausted with cold water: the infusion is concentrated by evaporation at a low

temperature, and mixed with yeast to destroy fermentable sugar. After fermentation, the liquid is boiled with a little lime to throw down tannin and nitrogenous matters, then evaporated to an extract and treated with animal charcoal, from which impure quercite is taken up by dilute spirit and crystallises on cooling. The crystals thus obtained contain salts of the alkalis and of calcium, which they retain obstinately. They are best purified by crystallisation from dilute hydrochloric acid. (2.) Or, better, the concentrated cold infusion of acorns is mixed with basic lead acetate, which throws down most of the impurities and colouring matter. The liquid is then fermented with yeast, freed from lead by means of sulphuric or carbonic acid and hydrogen sulphide, and evaporated. The white crystals thus obtained are finally purified by recrystallisation from dilute hydrochloric acid.

Quercite crystallises in clinorhombic prisms, which are usually hemihedral. Its action on polarised light is dextrorotatory: $[\alpha]_D = 24{\cdot}17$. Sp. gr. $= 1{\cdot}5845$ at 13°. It is soluble in about 11 parts of water at 12°, and in about 9 parts at 20°; insoluble in alcohol, ether, benzene, and chloroform. It melts at 225°. When heated at 100° for some days, quercite gradually loses water and approximates to the composition, $4C_6H_{12}O_5—H_2O$. When heated to 240° in a vacuum it yields about three-fourths of its weight of an anhydride, $C_{12}H_{22}O_9$: $2C_6H_{12}O_5—H_2O = (C_6H_{10}O_4)(C_6H_{12}O_5)$. This anhydride (which may be regarded as a compound of quercite and quercitan) melts at 228—230°, dissolves much less freely than quercite in water, and is nearly insoluble in alcohol and ether. Between 250 and 275° quercite loses more water and yields a sublimate of white, highly refracting, tabular crystals melting at 101—102°, the nature of which has not yet been determined. At 280—290° a totally different reaction takes place: the fused mass swells up enormously, giving off hydrogen, and the retort becomes filled with yellowish-green vapours of quinhydrone and hydroquinone, the latter of which condenses in long yellowish needles melting at 160°. This reaction is explained by the author as follows: a molecule of quercite losing 3 mols. of water is first converted into hydroquinone $C_6H_{12}O_5—3H_2O = C_6H_6O_2$: the hydroquinone by loss of H_2 gives rise to quinone which combines with more hydroquinone to form quinhydrone, $C_6H_4O_2(C_6H_6O_2)$.

Quercite, when fused with potash, evolves hydrogen and yields hydroquinone and quinhydrone, together with pyrogallol (or an isomeric substance), and oxalic and malonic acids.

Acetoquercites.—*Monacetoquercite*, $C_6H_{10}O_4(C_2H_4O_2)$, formed on heating quercite at 100° with glacial acetic acid in sealed tubes, is a white solid substance, difficult to crystallise. *Triacetoquercite*, $C_6H_6O_2(C_2H_4O_2)_3$, is readily formed on heating quercite at 130—140° with excess of glacial acetic acid containing 1 or 2 per cent. of acetic anhydride. It is a colourless amorphous solid of bitter taste and faint aromatic odour, insoluble in water, soluble in alcohol and ether. *Pentacetoquercite*, $C_6H_2(C_2H_4O_2)_5$, is obtained by heating quercite at 150° for many hours with excess of acetic anhydride. It is a colourless amorphous solid body, of very bitter taste, soluble in alcohol

and ether, and very sparingly in water. The acetoquercites are more volatile than quercite. When submitted to dry distillation they appear to yield *monacetoquercitan*.

Butyroquercites.—*Monobutyroquercite*, $C_6H_{10}O_4(C_4H_8O_2)$, formed on heating quercite at 100—115° with butyric acid, and is a semi-solid colourless body of bitter taste, soluble in ether and less freely in alcohol and water. *Tributyroquercite*, $C_6H_6O_2(C_4H_8O_2)_3$, is formed on heating quercite at 150—160° for many hours with excess of butyric acid. It is a syrupy uncrystallisable body, soluble in alcohol and ether. *Pentabutyroquercite*, $C_6H_2(C_4H_8O_2)_5$, is produced on heating the preceding compounds at 180° with a large excess of butyric acid. It forms a syrupy liquid of bitter taste, soluble in alcohol and ether, but scarcely so in water.

Chlorhydroquercites.—Quercite treated with dilute hydrochloric acid, even at 100°, is simply dissolved in large quantity; but the concentrated acid attacks it in such a manner as to substitute HCl for the elements of water; whilst the strongest acid (saturated at 0°) exerts at the same time a dehydrating action, resulting in the formation of quercitan or its chlorhydro-derivatives.

Monochlorhydroquercite, $C_6H_{10}O_4(HCl)$, is formed on heating quercite in the water-bath with excess of hydrochloric acid saturated at 10°. It is a white, crystalline substance, soluble in ether and in alcohol, and fuses at 198—200°. The mother-liquor contains *monochlorhydroquercitan*, $C_6H_8O_3(HCl)$, a viscid uncrystallisable body soluble in absolute alcohol. *Trichlorhydroquercite*, $C_6H_6O_2(HCl)_3$, is formed on heating quercite at 120—140° with excess of hydrochloric acid. It crystallises in long flattened needles melting at 155°. *Pentachlorhydroquercite*, $C_6H_2(HCl)_5$, is obtained by heating the last compound afresh with hydrochloric acid. It crystallises in slender yellow needles, fusible at about 102°. The mother-liquor contains monochlorhydroquercitan, which is, indeed, the chief product, corresponding in quantity with two-thirds of the quercite employed:

$$C_6H_{12}O_5 + HCl - 2H_2O = C_6H_8O_3(HCl).$$

Quercitan, $C_6H_{10}O_4$, is obtained by saponifying with baryta the chlorhydro-compound just mentioned, neutralising exactly with sulphuric acid, and evaporating. It is a colourless uncrystallisable and slightly deliquescent substance, soluble in water and in alcohol, insoluble in ether. When dissolved in 85 per cent. spirit it gradually takes up water, becoming converted into quercite.

Action of Hydrobromic Acid on Quercite.—Hydrobromic acid (sp. gr. 1·7) appears to act on quercite at 100° in the same manner as hydrochloric acid, producing a white crystalline substance soluble in water, and having the composition of *monobromhydroquercite*. But at higher temperatures the action is entirely different, the products being aromatic bodies, including benzene, phenol, hydroquinone, quinhydrone, quinone, and brominated derivatives of these last, which are still under examination.

Action of Hydriodic Acid on Quercite.—Quercite when distilled with hydriodic acid saturated at 0°, yields benzene (in quantity corresponding with half the quercite employed), phenol, iodophenol, quinone,

hydroquinone, oxyquinones, and volatile iodised products transformable into C_6H_{14}. The cold acid dissolves quercite freely, with slight rise of temperature, but no iodhydrate has been isolated.

In accordance with the foregoing results, quercite may be regarded as belonging either to the fatty or to the aromatic series of compounds. On the one hand, its behaviour with acids shows that it is a polyatomic alcohol capable of yielding a series of ethers of the general formula, $C_6H_2(H_2O)_5 + n\text{A}—n\text{H}_2\text{O}$, in which A represents a monobasic acid and $n = 1$, 3, or 5. Its decomposition by heat and by the action of potash, or of hydrobromic or hydriodic acid, indicate, on the other hand, its derivation from benzene: $C_6H_6—2H_2 + 2H_2O = C_6H_6O_2$ (hydroquinone); and $C_6H_6O_2 + 3H_2O = C_6H_{12}O_5$. It is the type of a group of bodies forming a connecting link between the two series. J. R.

Dinitrobenzophenone. By W. Staedel and E. Sauer (*Deut. Chem. Ges. Ber.*, **11**, 1747—1749).—When dinitrobenzophenone (m. p. 189°), which is most easily prepared by the oxidation of dinitrodiphenylmethane, is reduced with tin and hydrochloric acid, it is converted into the diamido-compound, whose hydrochloride forms with $SnCl_2$ a crystalline compound $(SnCl_2)_2 + C_{13}H_8O(NH_2)_2(HCl)_2$. The hydrochloride itself, $C_{13}H_8O_2(NH_2)_2(HCl)_2$, crystallises in large thick plates, which appear to form a basic compound when treated with water, but may be recrystallised without alteration from dilute hydrochloric acid. On treating this salt with ammonia, the base, $C_{13}H_8O(NH_2)_2$ is obtained as a white amorphous precipitate becoming crystalline on standing; it is decomposed by boiling water, and is best purified by dissolving in hydrochloric acid and precipitating with ammonia. It crystallises in white needles (m. p. 172°), and may be obtained from dilute aqueous solutions in small compact many-faced crystals.

The diamido-compound is converted by the diazo reaction into dioxybenzophenone, $C_{13}H_8O(OH)_2$; this compound crystallises from its aqueous solution in long slender needles (m. p. 210°). The properties of this compound and those of its benzoyl ether show it to be identical with that described by Staedel and Gail (*Ber.*, **11**, 746). Caro and Graebe (*Ber.*, **11**, 1249), Baeyer and Burkhardt (this Journal, 1878, 887), and Liebermann (this Journal, 1878, 886) have obtained the same compound in various ways, the melting point differing slightly from that given by the authors.

The action of zinc and hydrochloric acid on dinitrobenzophenone differs from that of tin and hydrochloric acid, and is still being investigated. P. P. B.

Synthesis of Aromatic Sulphones. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.* **11**, 2066—2070).—This paper describes the synthesis of a number of aromatic sulphones by the general reaction $R.SO_2Cl + R'H = HCl + RR'.SO_2$, the action requiring and being determined by the presence of aluminium chloride, as Friedel and Crafts have previously shown.

1. *Sulphobenzide*, $(C_6H_5)_2SO_2$, from benzene and benzene-sulphochloride. The yield amounted to 80 per cent. of the theoretical. Obtained in yellowish-white plates (m. p. 124°).

2. *Monochlorosulphobenzide*, $(C_6H_4Cl)_2SO_2$, from benzene chloride and sulphochloride. The yield was 87 per cent. of the theoretical. The compound crystallised from alcohol in brownish-white plates (m. p. 93°).

3. It is interesting as elucidating the mechanism of the general reaction, that bromobenzene and benzene-sulphochloride are mutually inert, no reaction occurring during a period of 14 days' heating, in presence of Al_2Cl_6.

4. Nitrobenzene and benzene-sulphochloride proved also to be without action on one another.

5. *Sulphotoluide*, $(C_6H_4.CH_3)_2SO_2$, from toluene and paratoluene-sulphochloride. The yield amounted to 87 per cent. of the theoretical. The compound is identical with that obtained by the action of sulphuric anhydride on toluene (Otto, *Annalen*, **154**, 193).

6. *Phenyltolylsulphone*, $C_6H_5.(C_6H_4CH_3).SO_2$, from toluene and benzene sulphochloride. This compound, obtained in yellowish rhombohedral plates (m. p. 125)°, proved to be identical with that obtained by Michael and Adair (*Ber.*, **11**, 116) by heating toluene and benzene-sulphonic acid together with phosphoric anhydride.

7. *Phenylxylylsulphone*, $C_6H_5.[C_6H_3(CH_3)_2]SO_2$.—From metaxylene and benzene-sulphochloride. Obtained in yellowish-white needles (m. p. 80°).

8. *Tolylxylylsulphone.*—From the product of the reaction of metaxylene and paratoluene-sulphochloride (m. p. 84°) traces only of a crystalline body were isolable.

9. *Sulphoxylide.*—The attempt to synthesise this compound according to the general reaction was not successful, neither could it be obtained by the action of sulphuric anhydride on xylene.

10. *Phenylnaphthylsulphone.*—From the product of the reaction of naphthalene and benzene-sulphochloride in presence of Al_2Cl_6, traces only of a crystalline body were isolated.

11. The reaction of benzene and its disulphochloride in presence of Al_2Cl_6, leading theoretically to a phenyldisulphone or a phenyl ether of benzenedisulphonic acid, yielded an amorphous mass, from which neither could be isolated. C. F. C.

Action of Sulphuric Hydroxychloride on Sulphobenzide. By R. Otto and A. Knott (*Deut. Chem. Ges. Ber.*, **11**, 2075—2076).—The chief product of the reaction of these bodies at 120° appears to be sulphobenzidesulphonic acid, formed according to the equation—

$$\left.\begin{matrix}C_6H_5SO_2\\C_6H_5\end{matrix}\right\} + SO_2{}^{OH}_{Cl} = HCl + \left\{\begin{matrix}C_6H_5SO_2\\C_6H_5SO_2OH\end{matrix}\right.$$

The authors are investigating this acid. C. F. C.

Disulphoxides of Benzene and Toluene. By C. Pauly and R. Otto (*Deut. Chem. Ges. Ber.*, **11**, 2070—2072).—Respecting the spontaneous decomposition, on keeping, of the sulphinic acids, even when pure and dry, according to the equation, $3RHSO_2 = R_2S_2O_2 + RHSO_3 + H_2O$ (*Ber.*, **10**, 2181), the authors find that it likewise occurs on keeping these acids over sulphuric acid in an atmosphere

of carbonic anhydride; that, therefore, atmospheric oxygen takes no part in the decomposition.

The authors have extended the proof previously given by them (*loc. cit.*) of the constitution of benzene disulphoxide being that of the phenyl ether of the unknown benzenethiosulphonic acid, similarly to the toluene compound, by realising the equation, $\left.\begin{matrix}C_6H_4.CH_3\,SO_2\\C_6H_4.CH_3\end{matrix}\right\}S + \left.\begin{matrix}(C_6H_4.CH_3)_2\\Zn\end{matrix}\right\}S_2 = [C_6H_4.(CH_3)SO_2]_2Zn + (C_6H_4.CH_3)_2S_2$. They also find that benzene disulphoxide reacts sharply with the free sulphydrate in alcoholic solution, according to the similar equation, $\left.\begin{matrix}C_6H_5SO_2\\C_6H_5\end{matrix}\right\}S + C_6H_5.HS = C_6H_5.HSO_2 + (C_6H_5)_2S_2$.

A further proof of the accuracy of this view is afforded by the oxidation of benzene disulphoxide by potassium permanganate to benzenesulphonic acid, which the authors have recently observed. Further attempts to synthesise the disulphoxide from benzene-zinc-mercaptide and benzene sulphochloride have, as previously, led to negative results; the following is the decomposition which actually occurs: $2C_6H_5SO_2Cl + 2(C_6H_5S)_2Zn = (C_6H_5)_2S_2 + (C_6H_5SO_2)_2Zn + ZnCl_2$.

The authors' attempts to prepare this body by the action of phosphorus pentasulphide upon the phenyl ethers of benzenesulphonic acid have also failed. C. F. C.

Tetranitro-oxysulphobenzide. By J. Annaheim (*Deut. Chem. Ges. Ber.*, **11**, 1668—1670).—It was shown (*Ber.*, **9**, 660) that two atoms of hydrogen in *dinitrosulphobenzide*, $(C_6H_3(NO_2).OH)_2SO_2$, could be replaced by bromine or iodine, and hence it was thought possible to obtain also the tetranitro-compound $[C_6H_2(NO_2)_2.OH]_2SO_2$.

Tetranitro-oxysulphobenzide, $[C_6H_2(NO_2)_2.OH]_2SO_2$, is obtained by the action at 70— 80° of red fuming nitric acid on dry dinitro-oxysulphobenzide; it may be purified by recrystallisation from hot water. It is a solid straw-yellow substance, with very bitter taste, and melting at 253°; on further heating it explodes. It is insoluble in most of the usual solvents, boiling water being the best medium for crystallisation; it is thus obtained in long needles. A small addition of hydrochloric acid will separate a further crop of crystals from the aqueous mother-liquors. The tetranitro-compound has well-marked acid properties, decomposing alkaline carbonates with ease. It is extremely soluble in boiling glacial acetic acid, but almost completely separates on cooling in beautiful needles, into the composition of which acetyl, has, however, entered.

Potassium tetranitro-oxysulphobenzide, $[C_6H_2(NO_2)_2OK]_2.SO_2$.—No crystalline water. Sparingly soluble in cold, moderately soluble in hot water; on cooling, microscopic reddish-yellow crystals separate, which explode on heating. *Sodium-compound*, $[C_6H_2(NO_2)_2ONa]_2.SO_2$. Easily soluble in cold or hot water, depositing after a long time minute yellow crystals. *Another sodium salt*, crystallising well (octahedra), and containing crystalline water, but very efflorescent, was obtained under certain circumstances. *Acetyl-compound.* Obtained by solution

of the tetranitro body in boiling glacial acetic acid. The *amido-compound* is obtained easily by treatment of the nitro-compound with tin and hydrochloric acid. W. S.

Discovery of Vanillin in Siam Benzoïn. By P. Jannasch and C. Rump (*Deut. Chem. Ges. Ber.*, **11**, 1634—1637).—Two parts of the benzoïn in very fine powder were mixed with one of calcium hydrate, made into a paste with water, and then boiled with twelve times the quantity of water. After decomposing with acid, and filtering off from the benzoic acid, the filtrate was shaken repeatedly with ether; on evaporating the ethereal solution the impure vanillin was obtained. After purification by means of hydrogen-sodium sulphite, and recrystallisation from water, crystals of vanillin were obtained almost colourless, and melting at 81°. The best solvent and purifying medium for vanillin was found to be petroleum spirit, boiling under 90°. In this the body is, in the cold, nearly insoluble, but abundantly soluble on boiling, and yields on cooling long needles in stellate clusters. It was noticed that in the final purification, a certain quantity of a crystalline substance different from vanillin was left behind, and did not dissolve in the sodium sulphite solution. This is to be further examined. W. S.

Action of Dehydrating Substances on Anhydrides. By S. Gabriel and A. Michael (*Deut. Chem. Ges. Ber.*, **11**, 1679—1683). —*Derivatives of Phthalylpropionic Acid.* As previously shown (*Ber.*, **10**, 1557; **11**, 1007; this Journal, **34**, 230, 734), the action of concentrated sulphuric acid on phthalylacetic acid gives rise to orthotribenzoylenebenzene.

Similar action on phthalylpropionic acid (the mixture being heated on the water-bath) gave rise to a body with empirical formula, $C_{20}H_{14}O_3$, which crystallises from alcohol in silky needles (m. p. 235—237°). A body of the above formula may arise thus—

$$2(C_{11}H_8O_4) - 2CO_2 - H_2O = C_{20}H_{14}O_3,$$

Phthalylpropionic acid.

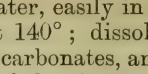
and the reaction may resolve itself into two stages, in the first of which the diketone, phthalyl-ethylidene, is first formed, and subsequently changed into the body in question, by dehydration, just as in the passage of acetone into mesityl-oxide.

$$\text{(I.)}\quad C_6H_4{=}(CO)_2{=}C_2H_3.COOH - CO_2 = C_6H_4{=}(CO)_2{=}C_6H_4.$$

$$\text{(II.)}\quad CO(C_6H_4)(C_2H_4)C\boxed{O.H_2}C_2H_2(CO)_2C_6H_4.$$

This compound is insoluble in acids and aqueous alkaline solutions. By fusing it with potash, an acid appears to be formed.

Phthalylpropionic Acid with Sodium-amalgam.—A solution of this acid in cold sodium hydrate solution yields benzoylpropiocarbonic acid (*Ber.*, **11**, 1015). This alkaline solution, treated with 2 per cent. of sodium amalgam, gives a body crystallising from dilute alcohol in shining colourless needles. It is tolerably soluble in hot, and but

slightly in cold water, easily in the ordinary solvents. It softens at 135°, and melts at 140°; dissolves in alkaline solutions, and expels carbonic acid from carbonates, and therefore has acid properties. Judging from analyses of the silver and barium salts, and from analogous observations with phthalylacetic acid, the empirical formula $C_{11}H_{10}O_4$ is resolved into  , a benzhydrylpropioncarbonic anhydride. On boiling this with baryta-water, the barium salt is formed, $C_6H_4<\begin{matrix}CH.OH.C_2H_4.COO\\COO\end{matrix}>Ba$.

Derivatives of Benzylidenephthalyl.—By the action of ammonia at 100° on deoxybenzoïncarbonic acid a nitrogenous compound is gradually formed. The resinous residue recrystallised from alcohol gave yellow scales, melting at 182—183°, insoluble in hot water, and affected neither by alkaline nor acid solutions. The formation of this neutral body proceeds in two stages—

$$COOH.C_6H_4.CO.CH_2.C_6H_5 + NH_3 = COOH.C_6H_4.C(NH).CH_2.C_6H_5 + H_2O$$

$$COOH.C_6H_4.C(NH)CH_2C_6H_5—H_2O = C_6H_4<\begin{matrix}C—CH_2.C_6H_5\\CO\end{matrix}>N$$. It is the *imido-deoxybenzoincarbonic anhydride.*

Mixture of Phthalic Anhydride and Isobutyric Acid with Sodium Acetate.—The mixture was heated in sealed tubes at 250°, carbonic anhydride was liberated, and a substance obtained, crystallising from hot acetic acid in long yellow needles (m. p. = 96°). It is soluble in hot alcohol and glacial acetic acid, scarcely in hot water. Is unaffected by potash solution at 100°, but at higher temperatures is decomposed with formation of an acid. The formula is—

$$C_{11}H_{10}O_2 = C_6H_4{=}(CO)_2{=}C{=}(CH_3)_2.$$ W. S.

Derivatives of Benzoic Acid. By P. Griess (*Deut. Chem. Ges. Ber.*, **11**, 1729—1734).—The author has already shown (*Ber.*, **5**, 855; *J. pr. Chem.*, **5**, 22) that meta-uramidobenzoic acid, when treated with nitric acid, yields three dinitro-acids, and that the corresponding para-derivative yields one only. Ortho-uramidobenzoic acid, when similarly treated, yields one dinitro-acid, resembling those already referred to, insomuch that when its aqueous solution is boiled, a nitroamido-acid is formed, which the author styles ε-nitro-amidobenzoic acid. This acid crystallises in pale yellow needles, slightly soluble in hot, and almost insoluble in cold water; it melts with partial decomposition between 265—270°. The barium salt, $(C_6H_3NO_2NH_2CO_2)_2Ba + 3H_2O$, crystallises in rhombic prisms or needles, and dissolves in water only in small quantities.

ε-Oxynitrobenzoic acid is formed on boiling the amido acid with potash, ammonia being evolved. It is difficultly soluble in hot water, separating out on cooling in slender white needles (m. p. 228°).

The acid barium salt, $[C_6H_3(NO_2)(OH)COO]_2Ba + 4H_2O$, is obtained in the form of bright yellow needles, which are tolerably soluble in

water. The neutral salt is obtained by treating the last-named salt or the acid with baryta-water, as a precipitate consisting of greenish-yellow needles having the composition $C_6H_3(NO_2)CO_3Ba$. This nitro-acid is identical with the nitrosalicylic acid, melting at 228°.

By reduction with tin and hydrochloric acid, ϵ-nitro-amidobenzoic acid yields a diamido-acid, from which a diphenylamine melting at 140° has been obtained, showing it to be identical with the α-diamido-benzoic acid described by the author, and which contains the groups $NH_2 : NH_2 : COOH$ in the positions 6 : 3 : 1. As ϵ-nitro-amidobenzoic acid is obtained from ortho-amidobenzoic acid, therefore its constitution is $C_6H_3(NO_2)(NH_2)COOH = [5 : 2 : 1]$, and that of the oxy-derivative is $C_6H_3(NO_2)(OH)COOH = [5 : 2 : 1]$. Hall and Wattenberg (*Ber.* **8**, 1215) have described two nitro-oxybenzoic acids obtained from salicylic acid, from which they have obtained two nitro-amido acids. Further Kruse (*Ber.* **10**, 1698) has shown that by replacing the NH_2 group of these acids by H, metanitrobenzoic acid is obtained. From this Hübner concludes that the constitution of these acids is either—

I. $C_6H_3(NO_2)(NH_2)COOH = [3 : 2 : 1]$ (m.p. 204°),
$C_6H_3(NO_2)(OH)COOH = [3 : 2 : 1]$ (m. p. 131°), or

II. $C_6H_3(NO_2)(NH_2)COOH = [5 : 2 : 1]$. $C_6H_3(NO_2)(OH)COOH = [5 : 2 : 1]$ (m. p. 228°).

From the identity of nitrosalicylic acid (m. p. 228°) with ϵ-oxynitrobenzoic acid, and also of their corresponding amido acids, it follows that the nitrosalicylic acid (m. p. 131°), and its corresponding nitro-amido acid (m. p. 204°), have the constitution represented by formula I.

Two oxy-acids are obtained by treating α- and γ-nitroamidobenzoic acids with potash. The α-acid, $C_6H_3(NO_2)(OH)COOH = [6 : 3 : 1]$, is obtained from its aqueous solutions in honey-coloured prisms or needles, which possess an acid taste, and are easily soluble in water, alcohol, and ether. Ferric chloride gives with its aqueous solutions a reddish-brown colour. It crystallises from water in crystals containing 1 mol. of water, which is expelled at 100°, the residue melting at 169°.

The barium salt, $C_6H_3(NO_2)CO_3Ba + 6H_2O$, is obtained by boiling the acid with barium carbonate; it crystallises in well-formed prisms, and is easily soluble in water.

γ-oxynitrobenzoic acid, $C_6H_3(NO_2)(OH)COOH + H_2O = [2 : 3 : 1]$, is more difficultly soluble in water than the α-acid, crystallising in four-sided yellowish-white leaflets, melting at 178°. By slow evaporation, it is obtained in tables and prisms. The aqueous solutions behave with ferric chloride like those of the α-acid; alcohol and ether dissolve it easily. The barium salt, $C_6H_3(NO_2)CO_3Ba$, forms reddish-brown rhombic plates, which dissolve in cold and hot water. This acid and its salts have the sweet taste characteristic of orthonitro-benzoic acid. P. P. B.

Constitution of Oxymesitylenic Acid. By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **11**, 2052—2055).—By the action of concentrated

hydrochloric acid at 200—205° on oxymesitylenic acid, the author has obtained liquid metaxylenol [1 : 3 : 4]: hence he assigns to the acid a corresponding constitution. He also treats this question by a second method, viz., by nitrating mesitylenic acid, converting the α-acid into the corresponding amido-acid, and this by the action of potassium nitrite into the oxy-acid. The latter he finds to be identical with the oxymesitylenic acid obtained from mesitol. Schmitz having established the constitution of α-amidomesitylenic acid by converting it into the corresponding metaxylidine, and the author that of oxymesitylenic acid as above, the conclusions of both are confirmed by the conversion of α-amido into oxymesitylenic acid.

The author also discusses the melting-point of β-nitromesitylenic acid, which Schmitz has observed to vary from 174—176° to 167—168°, and again 214—220°. He finds, on the other hand, that the acid obtained from the barium salt has a constant melting-point, 179°; but that when crystallised from boiling anhydrous alcohol it is raised to 223°, and again lowered to 179° by boiling with water. C. F. C.

Valonia and certain other Sources of Tannin. By H. Jahn (*Deut. Chem. Ges. Ber.*, **11**, 2107—2112).—Of the portion of the fruit of *Quercus ægilops* and *Valonia comata*, which constitutes the valonia of commerce, the author finds that the calyces contain 22·615 per cent. of tannin (mean of 12 analyses), the outside shells 36·60 per cent. (mean of 12 analyses), whilst the tannin estimated on the whole article was 25—26 per cent. The author has also made comparative determinations of the tannin in the several varieties of valonia, which establish the trustworthiness of the rough estimation of their commercial value by their colour, the higher-coloured varieties showing a higher percentage of tannin than the darker.

A sample of gall-nuts from the Peloponessus yielded 47·6 per cent. tannin (mean of 9 analyses). Two samples of pine bark, the one from Asia Minor, the other from Crete, were found to contain respectively 17·28 and 9·81 per cent. C. F. C.

Oxidation of Xylene-sulphamides. By Ira Remsen (*Deut. Chem. Ges. Ber.*, **11**, 2087—2092).—The author maintains, against the somewhat personal strictures of Jacobsen in a previous number, his original statement (*Ber.*, **11**, 1328), that on oxidising sulphamine-toluic acid with potassium permanganate, sulphisophthalic and not sulphamine-isophthalic acid is formed. He gives additional proof that the acid in question contains two atoms of hydrogen replaceable by metals, and has observed that it is absolutely free from nitrogen.

In conclusion he points to an inference from the mode of oxidation of the xylenols by fusion with potash, recently established by Jacobsen (*Ber.*, **11**, 375), viz., that as in these bodies the orthomethyl-group undergoes oxidation, so the action of potash on mesitylenesulphonic acid is, in the second stage, an oxidation of an orthomethyl-group, and consequently the resulting oxymesitylenic acid has the constitution $[OH : COOH : CH_3 : CH_3] = [1 : 2 : 4 : 6]$. This view is in harmony with the two characteristic properties of the acid, of volatilisation

with steam, and giving a coloration with ferric chloride, properties which seem, from the researches of Tiemann, to be generally characteristic of aromatic oxy-acids derived from salicylic acid. C. F. C.

Synthesis of the Compounds of Phenyl with Tin. By B. Aronheim (*Liebig's Annalen*, **194**, 145—175).—The processes attempted for the preparation of the phenyl-compounds of tin were analogous to those by which Michaelis and Gräff prepared the phenyl-derivatives of phosphorus, viz.:—By passing the mixed vapours of phosphorus chloride and benzene through a red hot tube:— $PCl_3 + C_6H_6 = C_6H_5PCl_2 + HCl$; and by treating mercury-diphenyl, $Hg(C_6H_5)_2$ with the chloride. By the first of these methods, the only products obtained were stannous chloride, diphenyl, and benzene. The chief reaction being $SnCl_4 + 2C_6H_6 = SnCl_2 + 2HCl + (C_{12}H_{10})_2$. The second process yielded a better result. The mercury-phenyl was prepared by treating phenyl chloride with sodium amalgam containing 2·7 per cent. of sodium. The yield was 46 per cent. of that required by theory. To prepare the derivatives of phenyl with tin, mercury-diphenyl was mixed with an equal weight of tin tetrachloride, and after addition of enough petroleum to cover the mixture, it was digested in a paraffin-bath for 12 hours. The product, after removal of the excess of stannic chloride by distillation, was slowly poured into water, care being taken to keep the mixture cool. The petroleum floats on the surface, and is drawn off; the lower stratum of liquid contains stannic chloride, hydrochloric acid, and stannophenyl chloride. The aqueous solution is heated to 85—90° on a water-bath; an oil sinks to the bottom, and as soon as it begins to change into a white powder on the surface, it is separated from the water. When allowed to stand it solidifies to a mass of white crystals of stannophenyl chloride.

When the aqueous solution from which the oil has been removed is heated for a longer time, it deposits (1) a mixture of stannophenyl chloride and stannophenyl hydroxychloride; (2) after a longer time, stannophenyl-hydroxychloride; (3) stannophenyl oxychloride, stanno phenyl oxide, $Sn(C_6H_5)_2O$, and stannic oxide. The first and third portions are converted into stannophenyl chloride by treatment with hydrochloric acid; the second is best washed with alcohol, and digested for a long time with water to convert it into the hydroxychloride, melting at 187°. The yield of these substances is about 33 per cent. of that required by theory.

Stannophenyl chloride, $Sn(C_6H_5)_2Cl_2$, forms colourless triclinic prisms (m. p. 42°). It boils at 333—337° with partial decomposition. It dissolves in all proportions in ether, and is easily soluble in alcohol and in petroleum. It is sparingly soluble in water with partial decomposition. It crystallises best from petroleum. With strong acids, it decomposes into stannic chloride and benzene.

Stannophenylhydroxyl chloride, $Sn(C_6H_5)_2ClOH$, prepared by the action of water on the chloride. It is insoluble in all ordinary solvents. It melts at 187°, and at a higher temperature evolves a smell of diphenyl.

Stannophenyl oxide, $Sn(C_6H_5)_2O$, prepared by the action of potash or soda, or ammonia, or its carbonate, on the chloride or hydroxy-

chloride. It forms a white powder, decomposing without fusion when heated. It is insoluble in all ordinary solvents.

The hydroxychloride treated with gaseous halogen-acids, yields corresponding derivatives. The chloride has already been described.

The *chlorobromide*, $Sn(C_6H_5)_2ClBr$, is a yellow oil solidifying suddenly after some days to a hard crystalline mass (m. p. 39°).

The *chloriodide*, $Sn(C_6H_5)_2ClI$, consists of clear prisms, melting at 69°. It is best crystallised from anhydrous ether. It is easily decomposed by water or heat. The best yield is obtained by treating the chloride with hydriodic acid gas:—$Sn(C_6H_5)_2Cl_2 + HI = HCl + Sn(C_6H_5)_2ClI$.

Stannophenyl dibromide, $Sn(C^9H_5)_2Br_2$, prepared by the action of hydrobromic acid on the oxide, is a thick colourless oil, solidifying instantaneously on addition of a crystal of the chlorobromide. It resembles the latter compound exactly in its properties. It melts at 38°.

The *diiodide* appears to decompose into tintetriodide and benzene, as soon as it is formed, thus:—$Sn(C_6H_5)I_2 + 2HI = SnI_4 + 2C_6H_6$.

Stannodiphenide diethoxide, $Sn(C_6H_5)_2(OC_2H_5)_2$, was prepared by treating sodium ethylate with the dichloride. An immediate white precipitate of a mixture of the oxide with sodium chloride was produced, and the filtrate, on evaporation, deposited small white crystals of the ethyl derivative. It is best purified by repeated solution in alcohol and evaporation over sulphuric acid.

Stannotriphenyl chloride, $Sn(C_6H_5)_3Cl$. This substance is formed by treating the dichloride with moist sodium-amalgam, or with ammonia:—

$$3Sn(C_6H_5)_2Cl_2 + 4NaHO = 2Sn(C_6H_5)_3Cl + 4NaCl + 2H_2O:$$
$$3Sn(C_6H_5)_2Cl_2 = 2Sn(C_6H_5)_3Cl + SnCl_4.$$

In the former reaction, some hydroxyl-chloride is produced at the same time; and in the latter, amido-chloride, $Sn(C_6H_5)_2NH_2Cl$, which decomposes with water into hydroxyl-chloride and ammonia. The *chloride* consists of white crusts melting at 106°, soluble in alcohol and ether. The *hydrate* is easily soluble in water and forms well-defined salts with acids, of which the author promises a description in his next memoir on the subject. W. R.

Naphthopicric Acid and some of its Derivatives. By T. Diehl and V. Merz (*Deut. Chem. Ges. Ber.*, **11**, 1661—1667).—*Trinitronaphthol* (*Naphthopicric Acid*), $C_{10}H_4(NO_2)_3OH$.—Best prepared by adding slowly to 1 part of dinitronaphthol ("naphthalene yellow") suspended in 10 to 15 parts of concentrated sulphuric acid, $1\frac{1}{3}$ to $1\frac{1}{2}$ times the theoretical amount of fuming nitric acid mixed with sulphuric acid. The mixture is left for ten days in a vessel placed in cold water, with repeated daily agitation. Yield, about 80 per cent. This long standing cannot be replaced by gently warming, or using greater excess of nitric acid. On one occasion, however, after 15 hours, a 70 per cent. yield was obtained, but the conditions being unknown, the

success could not again be realised. Experiments by R. Bourcart have shown that monohalogenised naphthalenes may be converted into trinitrohalogen derivatives. Naphthopicric acid forms a brilliant yellow colouring matter. The *potassium salt*, $C_{10}H_4(NO_2)_3.OK + H_2O$, was found to have this composition, as shown by Eckstrand.

Amidodiimidonaphthol Hydrochloride, $(C_{10}H_4.N_2H_2.OH)HCl$.—Obtained like the corresponding derivative from picric acid, by reduction of trinitronaphthol with tin and hydrochloric acid. The salt crystallises in green shining scales with metallic lustre, resembling "fuchsine" crystals. The solutions are of an intense dark red. Long boiling of the aqueous solutions causes decomposition, giving rise to the separation of a bluish-black flocculent precipitate. The dry compound also is not absolutely stable, thus resembling the amido-naphthalic acid and α-dioxynaphthoquinone. Wool and silk are dyed brownish-red by it.

Amidodiimidonaphthol Chromate. $(C_{10}H_4.N_2H_2.NH_2OH).H_2CrO_4$.—Obtained by adding potassium dichromate to solutions of the last-named salt, as a brownish-red precipitate, which is sparingly soluble in boiling water, giving a blood-red solution. *Platinochloride* $[(C_{10}H_4.N_2H_2.NH_2.OH)HCl]_2.PtCl_4$.—Heavy dark brown floccular precipitate, insoluble in water.

Amidodiimidonaphthol, $C_{10}H_4.N_2H_2.NH_2.OH$.—Obtained by treatment of solutions of the salts with alkaline hydrates or ammonia. Brownish-red flocks, consisting of fine needles, with metallic lustre. From alcohol, it crystallises in dark brown needles in clusters. Almost insoluble in water, cold benzene, and ether; in boiling alcohol easily soluble, in cold only moderately; yellow or dark red solutions. Ammonia dissolves the base to some extent, and therefore does not completely precipitate it from its saline solutions.

Triamidonaphthol Stannosochloride, $C_{10}H_4(OH)(NH_2)_3.3HCl + SnCl_2 + H_2O$.—Prepared by treatment of the base with tin and hydrochloric acid, or from the reduction-solution of the trinitronaphthol (see above). By concentrating the solution, the double salt crystallises out in warty groups of prisms (Eckstrand). By removing the tin with hydrogen sulphide, and concentrating the filtrate, white needles of the triamido-naphthol hydrochloride are obtained.

Triamido-naphthol Sulphate, $C_{10}H_4.(NH_2)_3.OH.H_2SO_4 + H_2O$.—Prepared by adding excess of sulphuric acid to the warm concentrated solution of the hydrochloride. The salt crystallises out on cooling in yellowish scales, which are stable when dry. It is easily soluble in water, the solution turning red in the air, quickly on agitation, and immediately on adding ferric chloride.

No *dioxynaphthoquinone* could be obtained from the amido- and amidoimido-compounds just described.

The *constitutional formula of the trinitronaphthol* was determined to be $[H_3.NO_2]C_4{=}C_2{=}C_4[(NO_2)_2OH.H]$.—The nitro groups were considered to be in both benzene rings of the nucleus, since no dioxynaphthoquinone was obtainable. Had the position of the hydrogen-substituents in the molecule of the trinitronaphthol, its amido-derivatives and the α-dioxynaphthaquinone been coincident, the amido-diimidonaphthol ought easily to have passed over into the α-dioxy-

quinone. Oxidation also of the trinitronaphthol in alkaline solution, with permanganate yields, not phthalic, but nitrophthalic acid melting at 213° (*See Annalen*, **160**, 56, and *Ber.*, **5**, 101). W. S.

Isoindol. By W. Staedel and Kleinschmidt (*Deut. Chem. Ges. Ber.*, **10**, 1744—1747).—In a former communication (*Ber.*, **10**, 1882), one of the authors stated that isoindol may be obtained in differently coloured crystalline varieties showing the same melting point. At the time, it was supposed that the colorations were due to the presence of impurity; since then, however, it has been found that the colorations are idiochromatic. One variety of isoindal crystallises in yellowish-green crystals, which, according to von Reusch, belong to the rhombic system, and have a prismatic form, when turned round the prismatic axis they appear successively coloured green, yellow, red, blue, and finally indigo-blue. These crystals have a fracture parallel to the end-face of the prism, each section behaving similarly to tourmaline. The blue variety and that crystallising in yellow needles have no action on polarised light. By crystallisation from glacial acetic acid, isoindol may be obtained in yellow leaflets; these may be converted into the blue variety by crystallising from alcohol and adding during the crystallisation a crystal of the blue variety. A red variety has also been obtained, which may be converted into the other varieties. The exact conditions under which the differently coloured varieties are obtained, are, as yet, not accurately known. The colours appear, however, to be due to the development of the different faces on the crystals. Concentrated hydriodic acid converts isoindol into a basic compound, melting at 125°; this when heated with acetic anhydride yields an acetyl compound, crystallising in bright yellow needles, melting at 190°. P. P. B.

Diphenyl Bases. By H. Schmidt and G. Schultz (*Deut. Chem. Ges. Ber.*, **11**, 1754—1755).—Hydro-azobenzene treated with hydrochloric acid yields benzidine and a new base; the former may be removed by means of sulphuric acid as an insoluble sulphate, the sulphate of the latter remaining in solution. The base, $C_{12}H_8(NH_2)_2$, from this soluble sulphate may be set free by the addition of an alkali. It is insoluble in water, but easily soluble in alcohol, from which it crystallises in needles. It melts at 45°, and boils at 363°. The acetyl compound $C_{12}H_8(NH.C_2H_3O)_2$ melts at 202°. When the base is treated with nitrous acid, a diphenol is obtained, melting at 156—158°. It crystallises in needles, and is converted into diphenyl by heating with zinc-dust. This observation, and the fact that the base can be made from benzoic acid, lead the authors to suppose that it is an isomeride of benzidine, which they style δ-diamido-diphenyl.

The authors hope to determine the relationship of Laubenheimer's dichloramido-diphenyl (*Ber.*, **8**, 1621), and Gabriel's dibromobenzidine (*Ber.*, **9**, 405), to one or other of the above bases. Further, the authors are determining the constitution of the diphenols prepared from the diamido-derivatives of diphenyl and of phenol-parasulphonic acid. P. P. B.

Some Coerulignone Derivatives. By H. Ewald (*Deut. Chem. Ges. Ber.*, **11**, 1623).—*Potassium hydro-coerlignone*, $C_{16}H_{16}K_2O_6 + 4H_2O$, prepared by boiling quickly a mixture of hydro-coerulignone and strong solution of potash until dissolved. The compound separates in small golden-yellow plates which rapidly oxidise in the air.

Hexmethoxyl-diphenyl, $C_{12}H_{14}(OCH)_6$.—Colourless silky needles, melting at 126°, and easily soluble in alcohol and in glacial acetic acid. Obtained from potassium hydrocoerulignone by heating it with dehydrated potassium methyl-sulphate and some methyl alcohol at 140° for six hours. $C_{12}H_4(OCH_3)_4(OK)_2 + 2(KSO_4.CH_3) = 2K_2SO_4 + C_{12}H_4(OCH_3)_6$.

Dibrom-hexmethoxyl-diphenyl, $C_{12}H_2Br_2(OCH_3)_6$.—Precipitated on adding bromine-water to the preceding compound in acetic acid solution. Crystallises from alcohol or glacial acetic acid in white needles (m. p. 138—140°). Soluble in concentrated sulphuric acid with blue colour.

Dichlor-hexmethoxyl-diphenyl, $C_{12}H_2Cl_2(OCH_3)_6$.—Obtained like the preceding, using chlorine-water. Crystallises from alcohol in colourless needles. W. S.

Eupitton and Pittacal. By A. Grätzel (*Deut. Chem. Ges. Ber.*, **11**, 2085—2087).—A recapitulation and comparison of the properties of these bodies with the view to establish their difference, in reply to a recent paper by Liebermann (*Ber.*, **11**, 1104). C. F. C.

Derivatives of Anthraquinone. By v. Perger (*J. pr. Chem.* [2], **18**, 117—192).—A. Amido-derivatives.—No amido-compound is obtained by heating monoxyanthraquinone with ammonia. Liebermann and Troschke (*Annalen*, **183**, 202) obtained amidoxyanthraquinone, $C_{14}H_6O_2(OH).NH_2$, by heating alizarin with ammonia. The author finds that a compound isomeric with this is simultaneously produced, and that if the reaction be conducted in sealed tubes at 180° to 200° a series of bodies is formed which may be distinguished by their solubilities in different menstrua, and by their tinctorial powers. The relative amounts of either amido-oxyanthraquinone and of the other compounds produced, depend chiefly on the quantity of ammonia employed, and in a lesser degree on the duration of the heating.

The new amido-compound, *amiderythro-oxyanthraquinone* or *β-alizarinamide*, $C_{14}H_6O_2.OH.NH_2$, may be obtained by treating the contents of the sealed tube, after filtering off solid matter, with hydrochloric acid, washing the precipitate, digesting with baryta, filtering (*α*-amido-oxyanthraquinone goes into solution), and decomposing the residue with acid. The pure compound is, however, more readily obtained by boiling *diamidanthraquinone* (see below) with potassium hydrate until ammonia is no longer evolved, and then adding hydrochloric acid to the violet-coloured liquid thus obtained. The new amido-compound separates in brownish flocks, which are perfectly pure.

β-alizarinamide crystallises from alcohol in brown needles; it sublimes at 150—153°. It is soluble in alcohol, with brown coloration;

in ether with yellowish-brown, in concentrated hydrochloric acid with yellow, and in concentrated sulphuric acid with brownish-yellow coloration. The salts of this compound differ from those of the α-compound in being very insoluble in water.

Both amidoxyanthraquinones yield alizarin on fusion with potash. When treated with nitrous acid, the β-compound yields β-monoxyanthraquinone, identical with that which Baeyer and Caro obtained by heating phenol with phthalic anhydride and sulphuric acid (Berl, *Ber.*, 1874, 968), whilst the α-compound yields α-monoxyanthraquinone, $C_{14}H_7(OH)O_2$. These two bodies are also characterised by marked differences in their acetyl-derivatives, which are produced by heating the amido-compounds with acetic anhydride in sealed tubes at 110—120°. *α-Acetamidoxyanthraquinone* crystallises in brilliant golden needles, melting at 170°, soluble in acetic acid, alcohol, and ether, readily soluble in alkalis, forming a brownish-yellow liquid. *β-acetamiderythroxyanthraquinone* crystallises in brownish-yellow needles melting at 242°; it is sparingly soluble in alkalis, forming a reddish-violet liquid.

Both acetyl-compounds when fused with potassium hydrate yield salts which are decomposed by acids, with reproduction of the original compounds: hence the author regards the replacement of hydrogen by acetyl as occurring in the amidogen rather than in the hydroxyl group, and assigns to the compounds the formula (α and β) $C_{14}H_6O_2.OH.NH(C_2H_3O)$.

When alizarin is heated with from 1·2 to 2·8 parts of ammonia (NH_3) at 170°, and that portion of the contents of the tube which is insoluble in ammonia is treated with alcohol, a blue liquid is obtained, from which water throws down a blue flocculent precipitate, which after drying resembles indigo in appearance. This substance on analysis gives numbers agreeing with the formula $C_{14}H_6O_2(NH_2)_2$. It is, however, different in many respects from the diamidanthraquinone which Böttger and Petersen obtained (*Annalen*, **160**, 148) by reducing dinitro-anthraquinone. The new *diamidanthraquinone* or *alizarin-diamide* is soluble in hydrochloric and sulphuric acids. It is converted into β-alizarinamide (see above) by boiling with aqueous solution of an alkali, or by treating its alcoholic solution with nitrous acid. This compound begins to decompose when heated to 130°. At higher temperatures it evolves ammonia, and finally chars without subliming. By long-continued boiling with water it is decomposed, with production of alizarin.

Of the other compounds produced by the action of ammonia upon alizarin, that which is insoluble in alcohol could not be obtained in a state of purity. Certain qualitative reactions are detailed, which show that this body differs in many respects from alizarin-diamide (see above), although it resembles it in being insoluble in ammonia. After removing alizarin-diamide and the other compound by solution in alcohol, a substance remained insoluble in all menstrua except concentrated sulphuric acid, and giving numbers agreeing with the formula for a condensation product of diamido-anthraquinone, viz., $(C_{14}H_6O_2).NH_2NH$.

From the fact that diamidanthraquinone readily exchanges one

NH_2 group for OH, and from other circumstances, the author regards the two NH_2 groups in this compound, and the OH and NH_2 groups in the amido-oxyanthraquinones, as having somewhat different functions. He gives the following formulæ :—

Monoxyanthraquinone.

$$C_6H_4(CO)_2C_6H_2\left\{\begin{matrix}OH\alpha\\H\end{matrix}\right.$$

Erythroxyanthraquinone.

$$C_6H_4(CO)_2C_6H_2\left\{\begin{matrix}H\\OH\beta\end{matrix}\right.$$

Alizarin.

$$C_6H_4(CO)_2C_6H_4\left\{\begin{matrix}OH\alpha\\OH\beta\end{matrix}\right.$$

Amidoxyanthraquinone. (α-Amide.)

$$C_6H_4(CO)_2C_6H_2\left\{\begin{matrix}OH\alpha\\NH_2\beta\end{matrix}\right.$$

Amiderythroxyanthraquinone. (β-Amide.)

$$C_6H_4(CO)_2C_6H_2\left\{\begin{matrix}NH_2\alpha\\OH\beta\end{matrix}\right.$$

Diamidanthraquinone (alizarindiamide).

$$C_6H_4(CO)_2C_6H_2\left\{\begin{matrix}NH_2\alpha\\NH_2\beta\end{matrix}\right.$$

The entrance of a single OH group into the anthraquinone molecule does not produce a body possessed of tinctorial power. The exchange of one OH for NH_2 in alizarin greatly reduces the tinctorial power of the compound, and when both OH groups are replaced by NH_2 this power is entirely destroyed.

B. Oxy- and Amidoxyanthraquinone Sulphonic Acids.—By cautiously fusing each of the anthraquinone-disulphonic acids with potassium hydrate, an *oxyanthraquinone-sulphonic acid* was obtained (Graebe and Liebermann, *Annalen*, **160**, 139). These acids were carefully purified and analysed. Their barium salts were also prepared and analysed, but it was not found possible to ascertain with certainty whether they were monoxy- or dioxy-acids. A considerable number of arguments are deduced in favour of the latter view, especially the fact that each of these acids yields a colouring matter on fusion with alkali, whereas neither of the monoxy-anthraquinone-sulphonic acids obtained directly from α- or β-monoxyanthraquinone (see below) yields a colouring matter on similar treatment; but further, one of the sulphonic acids obtained by treating alizarin with sulphuric acid (see below) likewise yields such a colouring matter, and this acid is undoubtedly a dioxy-acid, viz., $C_{14}H_5O_2(OH)_2SO_3H$.

If the acids produced by cautious fusion of the anthraquinone-disulphonic acids with potash be indeed dioxy-acids, then the following formulæ probably represent the steps in the process :—

$$C_{14}H_6O_2(SO_3H)_2;\ C_{14}H_6O_2(OH)SO_3H;\ C_{14}H_5O_2(OH)_2SO_3H,$$

Carrying the process a step further, we should expect to have $C_{14}H_5O_2(OH)_3$. The author shows that the product of the action of fused potash on these oxysulphonic acids is a trioxyanthraquinone

(flavopurpurin from α-acid, and anthrapurpurin from β-acid), and *not* alizarin, as stated by Graebe and Liebermann (*loc. cit.*).

The two anthraquinone-disulphonic acids themselves yield the same trioxyanthraquinones if the fusion with potash be carried sufficiently far. In this fusion, whether the intermediate products be regarded as monoxy- or as dioxy-acids, there seems to be at one part of the process an exchange of H for OH, during which the SO_3H group is not attacked.

Monoxyanthraquinone-sulphonic acids, α and β, $C_{14}H_6O_2(OH)SO_3H$, were prepared from α- and β- monoxyanthraquinone by treating with fuming sulphuric acid, saturating with baryta, purifying the barium salts, and decomposing by means of sulphuric acid (for details see original paper). The *same* acids were also obtained by the action of nitrous acid on the two amidoxyanthraquinone-sulphonic acids, obtained by acting on the two amidoxyanthraquinones by fuming sulphuric acid. Neither of these acids yielded a colouring matter on fusion with potash, but both were thus decomposed. Traces of a third acid were, however, obtained on treating α-monoxyanthraquinone with sulphuric acid, which appeared to form a colouring matter on fusion with alkali. The existence of such an acid is now being investigated by the author.

α-Monoxyanthraquinone-sulphonic acid, $C_{14}H_6O_2(OH)SO_3H$, forms yellow crystals which are with difficulty soluble in cold water, insoluble in ether, and somewhat soluble in alcohol. When heated at 150—160° with potassium hydrate, dioxyanthraquinone-sulphonic acid, $C_{14}H_5O_2(OH)_2SO_3H$, is produced, so that here again a replacement of H by OH occurs, the SO_3H group meanwhile remaining intact. *β-Monoxyanthraquinone-sulphonic acid* is best prepared from the lead salt by decomposing it with sulphuretted hydrogen. It dissolves in forming a yellow liquid, and behaves towards fused potash similarly to the α-acid.

Graebe and Liebermann (*loc. cit.*) obtained a sulphonic acid from alizarin, which they said again yielded alizarin on fusion with alkali. The author shows that when alizarin is treated with fuming sulphuric acid three *alizarin-sulphonic acids*, $C_{14}H_5O_2(OH)_2SO_3H$, are produced, that which is formed in greatest quantity yielding *purpurin*, but not alizarin, on fusion with potash; whereas the second acid is decomposed by fusion, without production of colouring matter; and the third acid, which is produced in small quantity only, is decomposed by continued boiling with water, with reproduction of alizarin. To the first of these acids the author gives the name of *alizarin-purpuro-sulphonic acid*. He regards this acid as probably isomeric with the di(?)oxyanthraquinone-sulphonic acid obtained by fusion of anthraquinone-disulphonic acid with potash (see p. 255).

The paper concludes with a sketch of the relations between anthraquinone-derivatives, according to the author's views. The following formulæ represent the more important relations. Roman letters are used to indicate varying functions of OH, NH_2, &c. :—

1. $C_6H_4(CO)_2C_6H_4$ = anthraquinone.
2. $C_6H_4(CO)_2C_6H_3.SO_3H_{II}$ = anthraquinone-monosulphonic acid.
3. $C_6H_4(CO)_2C_6H_3.OH_{II}$ = monoxyanthraquinone.

4. $C_6H_4(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\Big\}OH_{II}$ = alizarin; from (3) by direct exchange of H for OH.
5. $C_6H_4(CO)_2C_6H_3.OH_I$ = erythroxyanthraquinone.
6. $C_6H_4(CO)_2C_6H_2\begin{cases}OH_{II}\\NH_{2I}\end{cases}$ = amidoxyanthraquinone.
7. $C_6H_4(CO)_2C_6H_2\begin{cases}NH_{2II}\\OH_I\end{cases}$ = amiderythro-oxyanthraquinone.
8. $C_6H_4(CO)_2C_6H_2\begin{cases}NH_{2II}\\NH_{2I}\end{cases}$ = orthodiamidoanthraquinone.

(6, 7, 8: produced by the action of ammonia on alizarin.)

9. $SO_3H_{III}.C_6H_3(CO)_2C_6H_3.SO_3H_{II}$ = α- and β-anthraquinonedisulphonic acid.
10. $SO_3H_{II}.C_6H_3(CO)_2C_6H_3.SO_3H_{II}$
11. $SO_3H_{III}\left\{C_6H_3(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\right\}OH_{II}$
12. $SO_3H_{II}\left\{C_6H_3(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\right\}OH_{II}$ = dioxyanthraquinonesulphonic acids, corresponding to—
13. $OH_{III}.C_6H_3(CO)_2C_6H_3.OH_{II}$ = anthraflavic acid, and
14. $OH_{II}.C_6H_3(CO)_2C_6H_3.OH_{II}$ = isoanthraflavic acid.
15. $C_6H_4(CO)_2C_6H\begin{matrix}OH_{II}\\OH_I\\SO_3H_{III}\end{matrix}$ = alizarinpurpurosulphonic acid, which is also a dioxyanthraquinone acid. (See Nos. 11 and 12.)
16. $OH_{III}\left\{C_6H_3(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\right\}OH_{II}$ = flavopurpurin.
17. $OH_{II}\left\{C_6H_3(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\right\}OH_{II}$ = anthrapurpurin.
18. $C_6H_4(CO)_2C_6H\begin{matrix}OH_{II}\\OH_I\\OH_{III}\end{matrix}$ = purpurin.

(16, 17, 18: from the three dioxysulphonic acids, by exchange of SO_3H for OH.)

19. $C_6H_4(CO)_2C_6H_2\begin{cases}OH_{II}\\OH_{III}\end{cases}$ = purpuroxanthin.
20. $SO_3H\left\{C_6H_3(CO)_2C_6H_2\begin{matrix}\\OH_I\end{matrix}\right\}OH_{II}$ = alizarinsulphonic acid.
21. $SO_3H.C_6H_3(CO)_2C_6H_3.OH_{II}$
22. $SO_3H.C_6H_3(CO)_2C_6H_3.OH_I$ = monoxyanthraquinonesulphonic acids.

In Nos. 20, 21, and 22, SO_3H is with difficulty exchanged for OH.

23. $SO_3H\left\{C_6H_3(CO)_2C_6H_2\begin{cases}OH_{II}\\NH_{2I}\end{cases}\right.$
24. $SO_3H\left\{C_6H_3(CO)_2C_6H_2\begin{cases}NH_{2II}\\OH_I\end{cases}\right.$ = amidoxyanthraquinonesulphonic acids, giving Nos. 21 and 22 on treatment with nitrous acid.

M. M. P. M.

Anthracene-disulphonic Acid and its Conversion into Anthrarufin. By C. Liebermann and K. Boeck (*Deut. Chem. Ges. Ber.*, **11**, 1613—1618).—Zincke's method for preparing the anthracene-monosulphonic acids yielded only impure products, in short, chiefly disulphonic acids. The *quantity* of sulphuric acid taken was *too great*. Graebe and Liebermann had already observed the formation of the monosulphonic acid, with employment of a smaller proportion of sulphuric acid.

To prepare the disulphonic acid now described, anthracene was triturated with three times its weight of concentrated sulphuric acid, and the mixture digested for an hour, with stirring, at a very gentle heat. Several sulphonic acids are formed, but only one separates out on converting into the lead salts and evaporating.

To separate the sulphonic acid yielding chrysazin, the mixture of acid and anthracene is heated at 100° until about half of the anthracene is dissolved. On converting into lead salts and evaporating, the sulphonate yielding chrysazin first crystallises out, and, on further concentration, that yielding anthrarufin. Both series of salts are best distinguished by the conversion into their sodium salts (digestion of the lead salts with sodium hydrate). The sodium salt of the chrysazin series is more difficultly soluble in excess of sodium hydrate solution, and crystallises in almost needle-shaped lemon-yellow plates, whilst the more easily soluble salt of the compound leading to anthrarufin crystallises in small white silvery plates.

Compounds of the Series belonging to Anthrarufin.—*Sodium anthracene-disulphonate*, $C_{14}H_8(SO_3Na)_2 + x$Aq, forms silvery plates, easily soluble in water, giving a fluorescent solution. *Barium anthracene-disulphonate*, $C_{14}H_8(SO_3)_2Ba + 4H_2O$, precipitated from the solution of the sodium salt on adding barium chloride, forms white pearly plates, becoming yellow on drying at 170°. *Lead anthracene-disulphonate*, $C_{14}H_8(SO_3)_2Pb$, is a yellowish-white crystalline precipitate, which when once separated out, dissolves with great difficulty in water. *Anthracene-disulphonic acid* may be prepared by the action of hydrogen sulphide on the lead salt in solution. On evaporating, or adding concentrated sulphuric acid, it separates in crystalline microscopic needles.

Dioxyanthracene, $C_{14}H_8(OH)_2$.—The sodium salt is fused with five to six times its weight of potash, until hydrochloric acid causes a white flocculent precipitate in a dissolved sample: it is best purified by dissolving it in cold alcohol and adding water, when it gradually crystallises in needles. Its dilute solutions show a very strong blue fluorescence. Its solution in alkalis is yellow, and acids precipitate yellowish-white flocks. Strong sulphuric acid dissolves it with a reddish tint, turning green on warming. It decomposes at a high temperature without fusing or subliming, and is attacked by chromic or nitric acids, but no phthalic acid seems to be formed. This fact points to the constitutional formula $C_6H_3(OH)\begin{matrix}CH\\ \|\\ CH\end{matrix}C_6H_3(OH)$ for dioxyanthracene, and therefore the relation it bears to Zincke's monohydroxylated compounds is intelligible, and is similar to that subsisting between monoxyanthraquinone and anthraflavic acid.

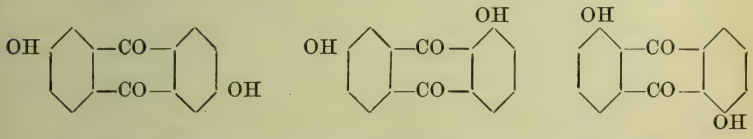
Dibenzoyl-dioxyanthracene, $C_{14}H_8(OC_7H_5O)_2$.—Prepared by boiling dioxyanthracene with benzoic chloride, and recrystallising from glacial acetic acid. Beautiful bright yellow needles (m. p. about 263°).

Diacetyl-dioxyanthracene, $C_{14}H_8(OC_2H_3O)_2$, obtained by boiling dioxyanthracene with acetic anhydride and sodium acetate, with ascending condenser, forms beautiful colourless plates (m. p. 196—198°).

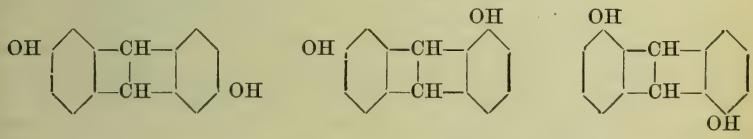
Diacetyl-dioxyanthrarufin, $C_{14}H_6O_2(OC_2H_3O)_2$. — Beautiful needles (m. p. 244°) resembling those of anthraquinone from the glacial acetic

acid solution. Obtained by boiling a glacial acetic acid solution of diacetyl-dioxyanthracene with chromic acid, $C_{14}H_{18}(OC_2H_3O)_2 + O_3 = H_2O + C_{14}H_6O_2(OC_2H_3O)_2$. It dissolves in sulphuric acid with splendid carmine-red colour, and the solution shows a well-defined absorption spectrum identical with that of anthrarufin. Boiling alkaline solutions remove the acetyl groups, whilst a dioxyanthraquinone dissolves with a yellow colour.

Anthrarufin, $C_{14}H_6O_2(OH)_2$.—Precipitated from the last-named solution with hydrochloric acid in yellow flocks. Soluble in concentrated sulphuric acid, with splendid carmine tint (m. p. 280°). It is identical with the anthrarufin of Schunck and Römer, obtained as a condensation product of oxybenzoic acid. The three isomerides of anthrarufin obtained by Schunck and Römer are the only ones theoretically possible from oxybenzoic acid, and have the formulæ :—



These correspond to the following three dioxyanthracenes, of which one belongs to these dioxyanthracenes :—



Oxyanthrarufin, $C_{14}H_8O_5$.—Identical with the oxidation product which Schunck and Römer obtained by fusing anthrarufin with potash. It dyes beautifully, like alizarin. Sublimes in red needles. It is the sixth isomeride now known of purpurin. It is not easy to distinguish from oxychrysazin (anthrarufin and chrysazin are also very similar); but it tinges sulphuric acid violet, whilst the oxychrysazin tint is much redder.

Anthrarufin obeys the general rule, that oxyanthraquinones with only one hydroxyl in each benzene-nucleus easily take up an oxygen-atom on fusion with potash, whilst those with several hydroxyls in one of the benzene nuclei do not show this inclination, and require oxidising agents to oxidise them. In the case of the latter bodies the oxidising partially destroys them, and partially reduces them to their leuco-derivatives, with characteristic colour changes. W. S.

Alizarin-blue. By C. Graebe (*Deut. Chem. Ges. Ber.*, **11**, 1646—1648).—Analyses of this compound (this Journal, 1878, Abs.) led to the formula $C_{17}H_9NO_4$. Reduction with zinc-dust left a base of the formula $C_{17}H_{11}N$. On heating nitroalizarin with glycerin and sulphuric acid, it is not only reduced, but a synthesis of alizarin-blue is effected, thus: $C_{14}H_7O_4(NO_2) + C_3H_8O_3 = C_{17}H_9NO_4 + 3H_2O + 2O$. It is the nitro-group which gives up the oxygen, for the alizarin-blue

unites both with bases to form salts, and also with acids. With sulphuric and hydrochloric acids it forms red needles, stable only in presence of excess of acid, and decomposed by water.

Analysis of the silver salt, which is a blue precipitate, insoluble in water, demonstrates that both hydroxyl groups of the nitro-alizarin are still intact in the "blue" obtained.

The base, obtained by reduction with zinc-dust, crystallises in small plates, which may be obtained colourless by sublimation. It is easily soluble in alcohol and ether, but not in water. The solutions have an extraordinary blue fluorescence. Vapour-density determinations by v. Meyer's method, using, however, amorphous phosphorus and sulphur instead of the latter alone (P_2S_5). Mean vapour density found = 8·19. The formula $C_{17}H_{11}N$ requires 7·93. The salts of the base are of a golden-yellow colour, and their solutions possess an intense green fluorescence, especially the dilute alcoholic solution.

The *hydrochloride*, $C_7H_{11}N.HCl$, crystallises from water in small prisms, and may be precipitated in slender needles on adding hydrochloric acid to the alcoholic solution of the base. Slightly soluble in alcohol and cold water, much more soluble in hot water. The *hydriodide*, $C_{17}H_{11}N.HI$, like the hydrochloride, is but sparingly soluble in water. The *sulphate*, $C_{17}H_{11}N.H_2SO_4$, obtained by precipitation of an alcoholic solution of the base with dilute sulphuric acid, forms needles, which are very soluble in hot, tolerably in cold water, and with difficulty in alcohol. *Picrate*, $C_{17}H_{11}N.C_6H_2(OH)(NO_2)_3$. By mixing alcoholic solutions of the base and picric acid, slender needles of this salt are obtained, which are insoluble in water, and only slightly soluble in alcohol. *Platinum salt*, $(C_{17}H_{11}N.HCl)_2PtCl_4$. Microscopic needles, insoluble in water. In colour of fluorescence the new base resembles acridine very closely. W. S.

Synthesis of Anthrarufin and Chrysazin from Anthracene. By C. Liebermann (*Deut. Chem. Ges. Ber.*, **11**, 1610—1613).—Little is known of the hydroxyl derivatives of anthracene, except that two anthrols were obtained by Zincke, by fusion of two isomeric anthracene-sulphonic acids with potash.

One or both of the two anthracene-disulphonic acids are obtained according to the temperature and proportions of anthracene and sulphuric acid employed. They can be separated by means of their lead salts. Both sulphonic acids give a series of beautifully crystallising salts. By fusing the acids with potash, the corresponding dioxyanthracenes are obtained.

With regard to the anthrols, the author states that the body proved by himself and Topf to have the constitution, $C_6H_4<\begin{matrix}CH\text{—}\\C(OH)\end{matrix}>C_6H_4$, since its hydroxyl group is not in the aromatic nucleus of the anthracene, belongs to a special class of compounds, viz., the anthranols. To this class also belongs the body which Giesel and the author obtained by reduction of quinizarin with hydriodic acid and phosphorus, viz., the hydro-anthracene-hydroquinone hitherto considered as—

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_2(OH)_2.$$

It was proved that the compound obtained by oxidation of the preceding is $C_{14}H_8O_3$, erythroxyanthraquinone, and accordingly the hydroanthracenehydroquinone has not the constitution above assigned to it, but the following, $C_6H_4<\begin{matrix}CH_2\text{——}\\CH(OH)\end{matrix}>C_6H_3(OH)$, as only a compound of *this*, and not one of the first given constitution, can yield mono-oxyanthraquinone by oxidation. By the reduction of quinizarin, therefore, both the ketone oxygens are not removed as before assumed, but only one, and an hydroxyl-oxygen atom. The properties of the compound, which may be termed *oxyhydroanthranol*, agree better with this view than with the former one, and readily explain how in the earlier described derivatives, one hydroxyl only was replaced. The lead salt is bibasic, and the barium salt, $(C_{14}H_{11}O_2)_2Ba$, which has also been analysed, likewise points to one hydroxyl.

It appeared to be of great importance to discover a general method by which the known oxyanthracenes might be converted into their corresponding oxyanthraquinones, which would afford some insight into their constitution: the oxyanthracenes themselves, however, from their phenol nature, have a great tendency to form resinous matters when treated with oxidation agents. Their acetyl-compounds, on the contrary, when oxidised with glacial acetic acid solution of chromic acid, readily yield acetylised oxyanthraquinones. In this way one of the anthracene-disulphonic acids may be converted into the dioxyanthraquinone recently named anthrarufin by Schunck and Römer, and obtained by them from oxybenzoic acid as a condensation product. The other anthracene-disulphonic acid, by a parallel series of reactions, yields another dioxyanthraquinone, viz., chrysazin, already obtained by the author and Giesel from chrysamminic acid.

Only about $\frac{1}{10}$th of the anthracene employed is converted into the sulphonic acid yielding chrysazin; about $\frac{1}{4}$th to $\frac{1}{3}$rd into that yielding anthrarufin. It has not yet been determined to what oxyanthraquinones the sulphonic acids remaining in the mother liquors belong, With reference to the sulphonic acid whose oxidation product was stated to be converted by fusion with potash into alizarin by Caro, Graebe, and the author, the latter now thinks it more probable that then they had in their hands anthracene-monosulphonic acids, passing over first into anthraquinone-monosulphonic acids, and then into alizarin on fusing with potash.

W. S.

Wax of Ficus Gummiflua. By F. Kessel (*Deut. Chem. Ges. Ber.*, **11**, 2112—2115.—This wax, which is used by the natives of certain districts of Java for illuminating purposes, is of a chocolate-brown colour, which it loses on treatment with boiling water, becoming almost white. It then consists of two bodies which are separated by taking advantage of the difference of their solubility in ether. The more difficultly soluble constitutes about $\frac{1}{20}$th of the crude material, melts at 62°, and has the empirical formula, $C_{27}H_{56}O$. It reacts with phosphorus pentachloride to form a chloride which is not decomposed by water, and with acetic chloride to form a crystalline acetate (m. p.

57°). It contains therefore an OH group, and is probably an isomeride of ceryl alcohol.

The more easily soluble, on the other hand, melts at 73°, and has the composition $C_{15}H_{30}O$. It reacts with phosphorus chloride and acetic chloride. The purified wax yields on dry distillation a crystalline body, which separates from its solution in petroleum in pearly scales; it melts at 62° and boils at 345—354°; its composition is represented by the empirical formula, $C_6H_{12}O$. It yields a crystalline acetate (m. p. 57°). C. F. C.

Investigation of Balsamum Antarthriticum Indicum. By B. Hirsch (*Arch. Pharm.* [3], **13**, 433—447).—The crude balsam appears as an opaque brownish liquid, saturated with small drops of water; it has a sp. gr. of 1·010 and an unpleasant rancid taste. When heated, the balsam becomes clear, owing to the loss of water, which amounts to 5·75 per cent., and the sp. gr. then rises to 1·016; heating causes also the formation of an unpleasant odour; at a strong heat, vapours are given off, but acrolein cannot be detected, so that glycerin would seem to be absent. The ash of the balsam contains iron. The balsam heated by itself does not ignite, but will burn from a wick. On shaking it with water, valeric acid is dissolved, leaving behind a mass which is soluble in alcohol. A portion is capable of saponification, another portion consisting of oil of resin, an oil indifferent to alkalis. Basic substances such as ammonia and lead oxide, combine readily with the balsam. If the balsam be extracted with alcohol of sp. gr. 0·892, a portion only is soluble, and this with hydrochloric acid forms a yellow oily substance, which solidifies to a plastic yellow mass soluble in ether. On comparison of these results with the reactions of gurjun balsam, it is found that the two are not identical.

E. W. P.

On Picoline and its Derivatives. By W. Ramsay (*Phil. Mag.*, October, 1876; October, 1877, and July, 1878).—I. Bases of the series, $C_nH_{2n-5}N$, have been obtained by the following methods:—

(1.) From the products of destructive distillation of bones (dippel-, or bone-oil), by Dr. Anderson.

(2.) From coal tar.

(3.) From the cinchona alkaloïds by distillation with potash or soda.

(4.) Pyridine was obtained by Perkin by reducing azodinaphthyldiamine with tin and hydrochloric acid.

(5.) From amyl nitrate by dehydration with phosphoric anhydride (Chapman and Smith).

(6.) Picoline was discovered by Claus among the decomposition-products of acrolein-ammonia when submitted to dry distillation.

(7.) Collidine was prepared by Bayer by a somewhat similar process, viz., by distillation of aldehyde-ammonia.

(8.) Bayer also obtained picoline by heating tribromallyl with alcoholic ammonia.

(9.) Huber oxidised nicotine, and distilled the resulting acid with lime; the distillate consisted of pyridine.

(10.) Dewar suggested that pyridine might be produced by the

mutual action of acetylene and hydrocyanic acid. The process was realised by the author. On passing a mixture of acetylene and hydrocyanic acid through a red hot tube, the reaction took place thus :

$$2C_2H_2 + HCN = C_5H_5N.$$

(11.) The author, in conjunction with Mr. James Dobbie, has ascertained that the acid produced by oxidising bases of cinchona-bark with potassium permanganate yields pyridine when distilled alone or with lime.

II. *Salts of picoline*, C_6H_7N.

Hydrochloride.—White deliquescent salt, best obtained pure by distillation. Melting point 160°.

Hydrobromide.—Like the former, melts at 187°.

The *hydriodide* decomposes when heated.

Derivatives of these Salts.—(*a.*) The *hydrochloride* absorbs chlorine when exposed to that gas, but evolves it on exposure to air. (*b.*) The *hydrobromide* unites with bromine at 190°, forming golden-yellow scales of the formula $C_6H_7N.Br_2.2HBr$. This body evolves bromine on exposure to air, and is sparingly soluble in water. (*c.*) The *hydriodide*, when partially decomposed by distillation, solidifies to a mass of reddish-brown needles, having the formula $C_6H_7N.I_2.2HI$. This body is decomposed by water and melts at 79°. It is soluble in alcohol and in ether, but not in carbon bisulphide.

Methochloride.—A deliquescent crystalline mass, crystallising from alcohol in needles, prepared by the action of silver chloride on the methiodide. Its platinum derivative, $(C_6H_7N.CH_3Cl)_2PtCl_4$, crystallises in small cubes.

Methiodide, $C_6H_2N.CH_3I$. — Prepared by direct combination of methyl iodide with picoline. A slightly deliquescent salt, crystallising from alcohol in long white needles, melting at 226·5—227°. This substance unites with iodine, forming the compound $C_6H_7N.I_2.CH_3I$; bluish-black feathery plates, melting at 129°. It is soluble in alcohol and in ether, but not in carbon bisulphide or in water.

Methonitrate, $C_6H_7N.CH_3NO_3$. — Obtained from the methiodide with silver nitrate. Transparent prisms, easily obtained an inch in length.

The *methydroxide*, prepared by adding silver oxide to the methiodide, decomposes when evaporated to dryness, leaving a red residue with a putrid smell.

Ethylene bromide, $(C_6H_7N)_2C_2H_4Br_2$.—Small prisms, melting at 276°. The chloride crystallises from alcohol in needles.

The compounds of picoline with allyl-chloride, iodide, &c., are all syrups, except the platinochloride, $(C_6H_7N.C_3H_5Cl).PtCl_4$.

Acetochloride.—A very deliquescent brownish crystalline body, of the formula $C_6H_7N.C_2H_3OCl$.

The *benzochloride* has similar properties.

Platinocyanide, $2C_6H_7N.Pt(CN)_2 2HCN.4H_2O$.—Large yellow rhomboidal crystals.

Tartrate $(C_6H_7N)_2.C_4H_6O_6$.—White needles, smelling faintly of picoline.

The *citrate* is a syrup; the *phosphate* is a crystalline mass, which

rapidly absorbs water; the *chlorate* forms thin diamond-shaped crystals. Picoline does not combine with acetic, formic, or chromic acids.

III. *Action of Chlorine on Picoline.*—When small quantities of picoline are thrown into a jar of chlorine, a yellow oil is produced, together with a large amount of hydrochloride. On addition of water the latter dissolves, while the former is converted into a white powder. From numerous analyses it was found to contain—

C, 25·81 p.c.; H, 2·91 p.c.; N, 5·66 p.c.; Cl, 49·17 p.c.,

and the oxygen, by difference, amounts to 16·48 p.c. The formula which most closely represents these numbers is $C_6H_7NO_3Cl_4$. This powder is very sparingly soluble in water, communicating to it the smell and taste of a hypochlorite; it also dissolves in alcohol and in glacial acetic acid, and decomposes when heated. With bromine, an analogous product is formed, together with hydrobromide, the dibromide of the hydrobromide, and picoline dibromide, $C_6H_7N.Br_2$, crystallising from chloroform in small interlaced needles. A similar compound of the formula $C_6H_7N.ClI$ was obtained by adding iodine monochloride to a mixture of picoline and chloroform. It crystallises in long yellow needles.

IV. *Decomposition Products of Picoline Platinochloride.*—By heating the platinochloride with water in a sealed tube at 170° for some days, two compounds are produced, which can be separated from each other by taking advantage of their different degrees of solubility. They are formed by the following reactions:—

$$(C_6H_7N.HCl)_2PtCl_4 = C_6H_7N.PtCl_4 + HCl + C_6H_7N.HCl;$$
$$(C_6H_7N.HCl)_2PtCl_4 = (C_6H_7N)_2PtCl_4 + 2HCl.$$

The compound $(C_7H_7N)_2PtCl_4$, is a bright yellow powder, moderately soluble in water, and the other compound, $C_6H_7N.PtCl_4$, is an insoluble dirty yellowish-green body. Neither of these substances evolves picoline when boiled with caustic alkalis.

V. *Dipyridine*, *Isodipyridine*, and *Dipicoline.*—Bases of the pyridine series are polymerised when left in contact with metallic sodium. The first of these, *dipyridine*, $C_{10}H_{10}N_2$, was discovered by Dr. Thomas Anderson; he had determined its vapour-density, the necessary temperature being obtained with a lead-bath; as the molecular weight of these compounds is only to be found by their specific gravity as gases, the author repeated this determination by means of the apparatus recommended by Victor Mayer, and found it to have the vapour-density 76·63. Theory requires 79, provided it has the formula $C_{10}H_{10}N_2$.

Isodipyridine.—A liquid boiling at 145—155° in a vacuum, and at 295—303° in air, was fractionated from the mother-liquor of the crystalline dipyridine. It has also the formula $C_{10}H_{10}N_2$. Its vapour-density at 444° was found equal to (1) 81·55; (2) 82·80, instead of 79°. Its sp. gr. is 1·08. It is a yellow oil, and does not solidify in a mixture of snow and salt, even on addition of crystals of dipyridine. It is sparingly soluble in water, but mixes in all proportions with alcohol and ether. Its *hydrochloride* forms hard white crystals; and

its *platinochloride* is a yellow crystalline precipitate. The compound with *methyl iodide* is a brilliant scarlet powder, insoluble in absolute alcohol and ether, but sparingly soluble in aqueous alcohol, and easily soluble in water, forming a nearly colourless solution. The *methyl-chloride* is a syrupy liquid, giving a yellow precipitate with platinum chloride, of the formula $C_{10}H_{10}N_2.2CH_3Cl.PtCl_4$.

Dipicoline, $C_{12}H_{14}N_2$.—A heavy oil, with a peculiar basic smell, prepared by treating picoline with sodium. It boils at 310—320°. It was separated by fractionation in a vacuum, when it boils at 165—175°. It is very sparingly soluble in water, but more easily with alcohol and ether. Its sp. gr. is 1·12. It is slightly volatile with water-vapour. Its vapour-density was found to be 97·99. Theory for $C_{12}H_{14}N_2$, 93. Its salts have little tendency to crystallise, but its platinic chloride, $C_{12}H_{14}N_2.2HCl.PtCl_4$, is a yellow crystalline powder.

The *methiodide*, $C_{12}H_{14}N_2.2CH_3I$, is a bright yellow powder, almost insoluble in alcohol and ether, but readily soluble in water, giving a colourless solution. The *methochloride* is a white crystalline salt. The *methylplatinochloride*, $C_{12}H_{14}N_2.2CH_3Cl.PtCl_4$, is deposited from water in yellow crystals. Iodine combines with the methiodide forming brown scales insoluble in carbon bisulphide, of the formula,

$$C_{12}H_{14}N_2.2CH_3I.I_6.$$

On treatment with bromine-water, dipicoline gives a bulky buff-coloured precipitate of the formula $C_{12}H_{13}BrN.2HBr$.

On oxidation with potassium permanganate, dipicoline yields a mixture of acids, which when heated evolve the smell of the polymerised bases. It is therefore probable that a polymeride of dicarbopyridenic acid is produced.

VI. *Oxidation of Picoline and Lutidine.*—It was discovered by Dewar that picoline, when oxidised with potassium permanganate, yields an acid of the formula $C_7H_5NO_4$, to which he gave the name *dicarbopyridenic acid*. The author investigated this acid and its salts; and having oxidised lutidine by a similar process, obtained at least other two acids, isomeric with Dewar's acid. He therefore names the acid obtained from picoline *α-dicarbopyridenic acid*, and prefixes the letters β and γ to two of those produced by oxidising lutidine.

The general method of preparing these acids is as follows:—25 grams of the base are boiled in a tinned iron vessel connected with an inverted condenser, with 250 grams of potassium permanganate, and 4 litres of water. When the permanganate has lost its colour, the liquid is distilled, to recover unoxidised base, and the distillate is used instead of water in the next preparation. The potassium salts are then evaporated to dryness, and exhausted with absolute alcohol in an apparatus by which the same alcohol is used over and over again. The salts soluble in alcohol are then dissolved in water, and fractionally precipitated with lead nitrate. The lead salt was then decomposed with sulphuretted hydrogen, the lead sulphide removed by filtration, and the filtrate evaporated. The *α-acid*, obtained in this way from picoline separated first in long hair-like needles; on recrystallisation from hot water, it deposited in plates resembling crystals of naphthalene, and those, on standing in their mother-liquor for some time,

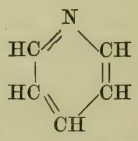
changed to short thick prisms. It has a sweet taste, but no smell. It is more soluble in alcohol than in water, and also dissolves in ether.

On oxidation lutidine gave the α-acid and also other two acids, which were separated by fractional crystallisation, one, sparingly soluble, separating out from its aqueous solution as a white crystalline powder, named β-dicarbopyridenic acid; and the other, a more soluble acid remaining in the mother-liquor of the β-acid distinguished as γ-dicarbopyridenic acid. Besides these acids, a very bitter acid substance remained in the mother-liquor of the γ-acid, which has not improbably the same formula.

Under the microscope the *β-acid* presents the appearance of truncated octahedrons, grouped in masses. It is more soluble in alcohol than in water, and dissolves sparingly in ether. It decomposes at 244—245°, evolving the odour of pyridine. Its vapour-density taken at the temperature of boiling sulphur was found equal to 29·22; that of a mixture of the products of decomposition as indicated by the equation, $C_5H_3N(COOH)_2 = C_5H_5N + 2CO_2$ is 27·8.

γ-Dicarbopyridenic acid crystallises in tufts of spear-like crystals, springing from a common nucleus. It has a satin-like lustre. Its solubility in water of 18° is 1·158 gram in 100 grams of water; it is easily soluble in alcohol and ether. The vapour-density of its decomposition-products was found to equal 28·4. It therefore seems to decompose in a manner similar to its isomeride.

These characteristics (see p. 267) are sufficient to prove that the three acids are not identical, but isomeric. They possess in common the property of evolving pyridine when heated, and of giving a dark red coloration with ferrous sulphate. If it be granted that pyridine has the "ring-form"—



it is evident that a number of isomeric acids (six in all) are theoretically possible.

General Conclusions.—1. Bases of the series $C_nH_{2n-5}N$ are tertiary bases; they are not attacked by nitrous acid; nor do they unite with more than one molecule of a halogen compound of an alcohol radicle.

2. They are unsaturated compounds, but have no great tendency to form addition-compounds. The addition-compounds are divisible into three classes:—(*a*) compounds in which the base combines directly with an acid to form a salt; (*b*) compounds in which the base unites with two atoms of a halogen, *e.g.*, picoline chloriodide, $C_6H_7N.ClI$; and (*c*) those in which a salt combines with two atoms of a halogen, in the pyridine series, as, for example, the diiodide of picoline methyl-iodide, $C_6H_7N.CH_3I.I_2$, and with six atoms of a halogen, as in the case of a hexiodide of dipicoline methiodide—

$$C_{12}H_{14}N.(CH_3I)_2I_6.$$

3. Like the paraffins, they are not attacked by acid oxidising agents

Comparative Tables of the Properties of the three Dicarbopyridenic Acids and their Salts.

α. Crystalline Forms.	β. Granular Microscopic Octahedra.	γ. Spear-shaped Crystals.
(1.) Hair-like needles. (2.) Plates resembling naphthalene. (3.) Short prisms.		
Solubility.		
Moderately soluble in water. More soluble in alcohol. Easily soluble in ether.	Slightly soluble in water. More soluble in alcohol. Sparingly soluble in ether.	Moderately soluble in water. Easily soluble in alcohol and ether.
Decomposing point, 237·5°.	244—245°	241—245°.
Salts.		
Ammonium Salt.—Small soluble plates.	Moderately soluble needles.	Soluble needles.
Calcium Salt.—Contains no water. Sparingly soluble. Small needles.	Contains $2H_2O$. Microscopic needles. Sparingly soluble.	Contains $2H_2O$. Small plates. Sparingly soluble.
Barium Salts.—Neutral salt. Contains H_2O, and resembles the calcium salt.	Sparingly soluble.	Soluble.
Acid Salt.—Very sparingly soluble.	—	—
Potassium Salts.—Neutral salt. Very soluble. Contains $1\frac{1}{2}H_2O$.	Soluble.	Soluble.
Acid Salt.—Globular masses, consisting of tufts of needles, radiating from a common centre.	—	—
Lead Salt.—Short prisms. Sparingly soluble.	White crystalline precipitate.	White crystalline precipitate.
Copper Salts.—(1.) Light blue needles. (2.) Dark blue prisms.	Light blue precipitate.	Whitish-blue precipitate.
Silver Salts.—(1.) Neutral Salt:—Bulky, white, insoluble, gelatinous precipitate. (2.) Acid Salt.—Ditto.	Very sparingly soluble crystalline precipitate.	Very sparingly soluble crystalline precipitate.
With Ferric Chloride.—No change of colour; a precipitate, even after addition of ammonia.	White flocculent precipitate, turning like ferric hydrate on addition of ammonia.	White flocculent precipitate, changed to ferric hydrate by ammonia.
Copper Sulphate.—No precipitate.	Whitish-blue precipitate.	Whitish-blue precipitate.
Methyl Ether.—Thick isolated crystals.	Deliquescent needles.	—
Chloride.—Crystalline mass. Melting point, 60·5—61°. Boiling point, 284°.	Crystalline mass. Melting point, 49°. Boiling point, 269—270°.	Crystalline mass. Melting point, 88—89°. Boiling point, 265°.

in the cold. They differ from paraffins by withstanding such action even at a high temperature; and this is probably owing to the increased stability given to the molecule by nitrogen, which renders them basic, and imparts to them the property of forming salts. The heat of formation of these bases is doubtless very high; and when a still greater amount of heat is evolved by their combination with acids, the sum of heat-units evolved by the union of the carbon, hydrogen, and nitrogen, plus that evolved by the formation of their salts, is probably greater than that evolved by their oxidation.

4. It is consequently only in alkaline solution that they can be oxidised. In this case, the amount of heat evolved by the acid formed by oxidation uniting with the alkali increases the sum of thermal units evolved by their oxidation to a number larger than that evolved during the formation of the base. The amount of heat evolved, moreover, is not increased by that arising from a union of the base with an acid.

5. At least three isomerides are formed by replacement of two atoms of hydrogen in pyridine by carboxyl, COOH. From analogy with benzene, and consideration of the greater complexity of the molecule of pyridine, it is highly probable that more than three exist. These acids are produced by oxidising picoline and its higher homologues, and probably also by oxidising pyridine. This behaviour is analogous to that of benzene: for benzene when oxidised yields acids containing more than six atoms of carbon. From picoline, C_6H_7N, it was to be expected that monocarbopyridenic acid, $C_5H_4N.COOH$, should be produced; this acid has been obtained only by the oxidation of nicotine; α-dicarbopyridenic acid is the only one produced in large quantity by the oxidation of picoline. When lutidine, C_7H_9N, is oxidised, a mixture of at least three isomeric acids of the formula $C_5H_3N(COOH)_2$ is formed. This would imply the existence of as many different isomeric lutidines: and indeed it is highly probable that such isomerides exist; for great difficulty is experienced in separating isomeric liquids, especially (as in this case) when the presumption is that their boiling points are almost identical.

6. These isomerides may be represented in graphic formulæ. A closed chain appears best suited to express the behaviour of the bases and the isomeric compounds derived from them. The author failed in several attempts to convert the dicarbopyridenic acid into its alcohol (from which he had hoped to obtain a base), owing to the instability of the acid at a high temperature and the small yield of aldehyde when the acid was distilled with calcium formate. It was hoped to achieve the formation of the base by the following stages:—

$C_5H_3N(COOH)$; $C_5H_3N(CHO)_2$; $C_5H_3N(CH_2.OH)_2$; $C_5H_3N.(CH_2Cl)_2$; and $C_5H_3N(CH_3)_2$.

From similar reasons, an attempt to prepare lutidine, C_7H_9N, by distilling the methyl-ether of the α-acid proved abortive; in every case, pyridine was formed. In spite of these failures, it appears probable that picoline is *methyl-pyridine*, lutidine *dimethyl-pyridine*, &c., the presence of nitrogen, as conjectured in (3), giving stability to the

molecule, and preventing the oxidation of the methyl-groups to carboxyl.

7. On treatment with sodium, these bases are polymerised, no hydrogen being evolved by the action of the sodium on the base. An addition-product is consequently formed, probably by two atoms of sodium being taken up by each molecule of base; on coming into contact with a fresh molecule of base, the sodium leaves the first molecule, which has thereby its affinities left free for union with another similarly placed. It is very doubtful if any *compound* of picoline and sodium is formed. Certainly sodium does not combine with dipicoline: for that base can be freed from water by heating it to a high temperature with metallic sodium.

8. In conclusion, the author calls attention to the analogy between the furfural and pyridine groups. That they are closely related appears very probable. An attempt to effect the conversion of furfural, $C_5H_4O_2$, into pyridine through the following series of reactions, failed owing to the instability of furfuryl chloride.

$C_5H_4O_2$.	$C_5H_6O_2$.	C_5H_5OCl.	$C_5H_5O.NH_2$.	C_5H_5N.
Furfural.	Furfuryl alcohol.	Furfuryl chloride (unknown).	Furfurylamine (unknown).	Pyridine.

The furfural group, from its unstable nature, is probably analogous to the higher homologues of acetylene, and is best represented by an open chain; whereas the pyridine group, from its stability, and from the number of isomeric derivatives obtained from it, is, like benzene, best represented by a closed chain. W. R.

Absorption-Spectra of Solutions of Brucine, Morphine, Strychnine, Veratrine, and Santonine in Concentrated Acids. By A. Meyer (*Arch. Pharm.* [3], **13**, 413—416).—This paper contains little more than drawings of the different absorption-spectra produced by the above alkaloïds when dissolved in different proportions in sulphuric, hydrochloric, and nitric acids. E. W. P.

Further Remarks on Alstonia Constricta. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1753—1754).—In a former communication (*Ber.*, **11**, 1546) the author doubted the presence of quinine in the bark of *alstonia;* this is corroborated by Baron von Müller in Melbourne, who distinctly denies the presence of quinine in the bark of this plant.

P. P. B.

Contribution to a Knowledge of the Alkaloïds of Ergot. By T. Blumberg (*Pharm. J. Trans.* [3], **9**, 23—25; 66—68; 147—148). The author, after summarising the results of other investigators, proceeds to describe his own experiments and their results. The solution in which ecboline and ergotine are said to exist is the filtrate obtained after precipitation of sclerotic acid. This filtrate, having first been treated with lead acetate, and the excess of lead removed by hydrogen sulphide, yielded a precipitate with mercuric chloride; this precipitate should, according to Wenzell, contain ecboline, and the filtrate ergotine.

From the author's experiments, a detailed description of which is

given, it appears, however, that the alkaloïds can be almost completely precipitated by mercuric chloride from a concentrated extract of ergot, but cannot be entirely freed from mineral matter. The amount of ash may possibly be due to the presence of lactates, when the alkaloïd is contaminated with lactic acid; it is also possible that the alkaloïd has the property of combining with inorganic bases. Finally, the author comes to the conclusion that "ecboline" and "ergotine" represent one and the same alkaloïd.

Picrosclerotine.—Sclererythrin, prepared by Dragendorff's method (*Archiv. f. experim. Path. und Pharmacolog.*) is contaminated with picrosclerotine and fuscosclerotic acid; it may be separated from these by precipitation from its alcoholic solution with lime-water. The fuscosclerotic acid and picrosclerotine which remain in solution are then separated by addition of sulphuric acid and agitation with the fuscosclerotic acid being dissolved; any picrosclerotine which may be taken up is removed by converting the fuscosclerotic acid into the ammonium salt, which is soluble in water, whilst the picrosclerotine dissolves only with difficulty. Picrosclerotine is, however, easily dissolved by water acidulated with acetic acid. The author has prepared a quantity of picrosclerotine from residues obtained in the preparation of sclererythrin, and has observed its action on frogs, on which it acts as a poison. To extract it from the residues, they were moistened with an aqueous solution of tartaric acid, and kept during 24 hours at a temperature of 40°; they were then exhausted with 85 per cent. alcohol in a percollator, and after distilling off the alcohol, the residue was mixed with sufficient water to allow the fusco- and erythro-sclerotic acids to be removed by filtration. On adding ammonia to the filtrate after concentration, a precipitate was produced which was almost completely soluble in acetic acid; the liquid contained picrosclerotine, as the experiments on frogs proved. Attempts were made to obtain picrosclerotine which should be wholly soluble in acetic acid; but these failed, as after each evaporation of the alcohol an insoluble residue was obtained; this appears to be due to decomposition of the alkaloïd, as it increases if the latter be kept for some time. Under these circumstances also it appears to act less energetically as a poison. A solution of picrosclerotine heated with strong sulphuric acid assumes first a rose, and finally a violet tint; with concentrated acid it becomes violet-coloured in the cold; with Fröhde's reagent a solution of the alkaloïd was coloured violet-blue at the ordinary temperature; when heated, it became first violet, and then green. The author considers that the insoluble residue which was obtained each time that the alcoholic solution of picrosclerotine was evaporated, and gave a brown solution with potash and sulphuric acid, agrees in all its properties with the ergot resin examined by Ganser. E. W. P.

Cantharic Acid and a Hydrocarbon, C_8H_{12}. By J. Piccard (*Deut. Chem. Ges. Ber.*, **11**, 2120—2124).—This is a continuation of the author's investigation of the derivatives of cantharidin (*Ber.* **10**, 1504). Cantharic acid, there described as a strong monobasic acid, having the same empirical composition as cantharidin, $C_{10}H_{12}O_4$, is

deposited in large prisms (orthorhombic, 1·62 : 1 : 0·74) by the slow evaporation of its aqueous solution.

The normal copper salt of this acid, $Cu(C_{10}H_{11}O_4)_2$, crystallises in small blue needles, which are difficulty soluble in water. The normal potassium salt crystallises in slender needles. It reacts with ethyl iodide to form an ethereal salt, which boils at about 300°. Barium cantharate yielded on dry distillation (400°) a hydrocarbon, C_8H_{12}, and a small quantity of xylene, with formation of carbonic oxide and anhydride. The residual mass was found to contain, in addition to carbonate, the barium salts of two volatile acids, apparently butyric and xylylic. Cantharic acid, intimately mixed with excess of quicklime, and subjected to dry distillation, yielded 50 per cent. of its weight of an aromatic liquid, consisting chiefly of the hydrocarbon C_8H_{12}. This body, purified by rectification, boils at 134—135°, has a strong odour of turpentine, and absorbs oxygen rapidly from the air. The density of its vapour was found to be 3·68 (calc. for $C_8H_{12} = 3·73$). The author regards it as a lower homologue of terpene, and proposes for it the name *cantharene*. The formation of this body from cantharic acid takes place according to the empirical equation, $C_{10}H_{12}O_4 = C_8H_{12} + 2CO_2$.

Cantharic acid being, however, monobasic, the elimination of $2CO_2$ from its molecule leads to the inference that it is, like terebic acid, the anhydride of the unknown (dicantharic) acid,

$$H_4.C_6H_4(CH_2.OH).CH(COOH)_2,$$

which would be thus decomposed—

$$H_4.C_6H_4(CH_2.OH).CH(COOH)_2 = 2CO_2 + H_4.C_6H_4\begin{matrix}CH_2\\|\\CH_2\end{matrix}.$$

Assuming further that cantharene is dimethylbenzene dihydride, we arrive at a close analogy of this body to terpene. The formation of other products is referable to secondary decompositions.

C. F. C.

Formulæ of Rhamnetin and Xanthorhamnin. By C. Liebermann and C. Hörmann (*Deut. Chem. Ges. Ber.* **11**, 1618—1622).—In their work with rhamnodulcite (*Ber.*, **11**, 952), the authors collected considerable amounts of xanthorhamnin and rhamnetin, and have now prepared a number of derivatives, for the chief purpose of determining the formulæ of these bodies more positively. It is concluded that the formula $C_{12}H_{10}O$ given by Schutzenberger is the correct one, and that two of the five oxygen-atoms belong to hydroxyl-groups.

Rhamnetin, $C_{12}H_{10}O_5$.—Xanthorhamnin was dissolved in water, and heated with dilute sulphuric acid on the water-bath, when rhamnetin soon began to deposit in small needles. It crystallises from phenol in yellow needles.

Acetyl-rhamnetin, $C_{12}H_8O_3(OC_2H_3O)$.—Rhamnetin and anhydrous sodium acetate were boiled with acetic anhydride, with ascending condenser, until dilute alkali ceased to colour a portion of the crystallised product. The body crystallises from alcohol to which one-tenth acetic anhydride has been added, in white silky needles (m. p. 183—

185°). This method of acetylising is much preferred to the one with pure acetic anhydride, and proceeds very easily. No work with sealed tubes is needed as with the old method. The sodium acetate added seems to bring about the formation of the sodium salt of the substance, which then reacts with the acetic anhydride. As diacetylrhamnetin and triacetylrhamnetin give calculated numbers very near together, the propionyl and benzoyl-compounds were investigated to settle the number of acid radicles entering into combination.

Propionylrhamnetin, $C_{12}H_8O_3(OC_3H_5O)_2$.—Light yellow needles, melting at from 158—162°. Prepared like the acetyl-compound, but using sodium propionate and propionic anhydride.

Benzoylrhamnetin, $C_{12}H_8O_3(OC_7H_5O)_2$.—Small silky needles, almost colourless; easily soluble in glacial acetic acid, with difficulty in chloroform and alcohol (m. p. 210—212°). Prepared by heating one part rhamnetin with four of benzoic anhydride at 150°.

Dibromorhamnetin, $C_{12}H_2Br_2O$.—Prepared by brominating rhamnetin suspended in glacial acetic acid. Beautiful yellow needles, easily soluble in hot alcohol and glacial acetic acid, and also in benzene. Soluble in alkalis with yellow colour. It dyes like rhamnetin, only a little redder.

Dibromacetylrhamnetin, $C_{12}H_7Br_2(C_2H_3O)$.—Prepared from dibromrhamnetin, acetic anhydride, and sodium acetate, as above mentioned. White shining needles, becoming yellow at 200° (m. p. 211—212°).

Xanthorhamnin, $C_{48}H_{66}O_{29}$ (?).—This formula agrees better with the results obtained than the formula $C_{24}H_{32}O_{14}$ given by Schützenberger. The efforts to confirm the formula were not very successful, only this much is certain, that xanthorhamnin contains for 1 mol. rhamnetin 2 mols. of isodulcite.

Potassium-xanthorhamnin, $C_{48}H_{62}K_4O_{29}$.—Prepared by the action of alcoholic potash on an alcoholic solution of xanthorhamnin; is a yellow powder.

Dimethylrhamnetin, $C_{10}H_8O_5(CH_3)_2$.—Prepared by heating the above potassium salt with excess of potassium methyl sulphate and some absolute methyl alcohol at 120—130° for 10 hours. It is soluble in alcohol, and crystallises therefrom in almost colourless needles (m. p. 156—157°). Potassium-xanthorhamnin, therefore, by this reaction passes over, with separation of isodulcite, into potassium-rhamnetin, which then becomes methylated.

Xanthorhamnin is also similarly converted into rhamnetin by simply heating to over 100°. The change proceeds slowly at 130°, more quickly at 160°. W. S.

Albuminoïds of Gourd Seeds. By J. Barbieri (*J. Prakt. Chem.* [2], **18**, 102—116).—Vegetable vitellin was prepared from the above seeds, both by Weyl's method and also by Ritthausen's (see *Pfluger's Archiv.*, Bd., **12**, *Zeitchr. f. Phys. Chem.* Bd. **1**, 72), seeing that Weyl's method differs very much from Ritthausen's, and that the former seems to take exception to the method employed by the latter. A comparison was then made of the results of analyses of the products

thus obtained by the two methods. The comparative results follow:—

Vegetable Caseïn prepared by Ritthausen's Method.

C.	H.	N.	S.	O.	Ash.
51·31	7·49	18·15	0·55	22·50	1·20

Vegetable vitellin, by Weyl's Method.

	C.	H.	N.	S.	O.	Ash.
(A.)	51·36	7·58	17·86	0·54	22·66	1·12
(B.)	51·88	7·51	18·08	0·60	21·93	1·11

The preparation B was obtained from another kind of gourd. The process was also a little modified, in that the purification was somewhat extended. The amount of myosin present is very small in comparison with that of the vitellin. It is seen that, in spite of Weyl's criticism of Ritthausen's method, there is no sensible difference in the composition of the products.

The author's analyses of the vitellin of the gourd differ very little from those of Weyl on the vegetable vitellin in para-nuts, viz.:—

	C.	H.	N.	S.	O.
Per cent.....	52·43	7·12	18·10	0·55	21·80

W S.

Analytical Chemistry.

Use of Phenol-phthaleïn in Titration. By H. C. Vielhaber (*Arch. Pharm.* [3], **13**, 410).—Phenolphthaleïn is useless as an indicator of neutrality when bicarbonates are present, as it has no action on the bicarbonates; it is therefore necessary to avoid the formation of bicarbonates during neutralisation. E. W. P.

Analysis of Boiler Feed-Waters. By W. F. K. Stock (*Chem. News*, **39**, 5—7).—The following are the characteristics of a good boiler water. (1.) Freedom from any very appreciable quantity of suspended mineral matter. (2.) Absence of any trace of mineral acids or of acid salts, or corrosive salts of any kind. (3.) Absence of oily or fatty substances. (4.) A good boiler water should not contain more than 30 grains of solids per gallon, and not more than half of this should precipitate on boiling under pressure. The following method has been devised by the author as furnishing in a very short time most trustworthy information as to the character of any given water generally:—

1. The suspended matter is determined by filtering 700 c.c. of the water through tared papers, washing the residue, drying at 110°, weighing, then burning and weighing again.

2. The examination for free mineral acids consists in testing the

water after filtration (if necessary) with dilute cochineal tincture and determining the acid so found with decinormal soda. If corrosive salts are suspected, they are best arrived at by evaporating the water and trying the action of the concentrated liquid on a weighed strip of pure iron.

3. Oil or fat is determined by evaporating 350 c.c. on a water-bath (with the addition of one or two drops of dilute sulphuric acid) to about 70 c.c., cooling, agitating with ether, decanting the ethereal portion into a weighed capsule, evaporating over a water-bath, and weighing.

4. The proportions of solids deposited on boiling under pressure, and solids retained in solution on boiling under pressure, are found by taking an observation of the total solid matter the water contains and boiling 700 c.c. for three hours in a flask, connected by an india-rubber stopper with an inverted Liebig's condenser well fed with cold water. After cooling, the water is run through a dry filter, and 70 c.c. are evaporated at 100° as before. The difference between the weights of the two residues gives the solids deposited on simply boiling. To this must be added the calcium sulphate contained in the boiled and filtered water, since it is practically insoluble at a pressure of one atmosphere of steam. The calcium oxide is determined in 350 c.c. of the boiled and filtered water, calculated into dry sulphate, and added on to solids depositing on boiling. The difference between the number so obtained and the total solids, gives the solids remaining dissolved on boiling under pressure, which solids are of account only in as far as they augment the boiling point of the residual water. It is obvious that if a water contains any free acids, other than carbonic acid, the latter part of the process may be omitted.

In conclusion, it is stated that the boiling of water in a thin glass flask forms an excellent method of judging of its scale-forming qualities, and it is quite remarkable to note the various peculiarities of deposits so obtained. D. B.

Estimation of Nitric Acid in Well-Water. By J. M. Eder (*Zeitschr. Anal. Chem.*, 1878, 434—438).—Wagner's method of estimating nitric acid by heating with chromic oxide and soda in a stream of carbonic anhydride and determining the amount of chromic acid formed, becomes inapplicable in the presence of organic substances. Wagner proposed destroying the organic bodies by potassium permanganate before applying the process. A litre of the water is made alkaline with pure soda, boiled, and a slight excess of permanganate added. It is then evaporated down to about 30 c.c., with addition of permanganate sufficient to maintain a reddish tint. After cooling it is acidified with dilute sulphuric acid and permanganate added, so as to maintain a pale rose tint for half an hour: slight excess of barium hydrate is added, and then excess of sodium carbonate. The filtrate, thus freed from sulphuric acid and barium, is evaporated to dryness, and the residue is employed for the estimation.

The author tested this method against that of Tiemann on a well-water which contained much organic matter. The average result yielded by Tiemann's process was 0·192 gram of nitric acid per litre, whereas

Wagner's process yielded only 0·1835. This loss must arise either from oxidation-products or from incomplete destruction of the organic matter. The author recommends Wagner's modified process for well-waters, but he finds that it is inapplicable in the case of vegetable extracts, since there was always sufficient organic matter undestroyed to change some potassium chromate into chromic oxide. Tiemann's process is however more rapid and yields more accurate results. F. C.

Estimation of Phosphoric Acid as Ammonium Phospho-Molybdate. By R. Finkener (*Deut. Chem. Ges. Ber.*, **10**, 1638—1641).—It is found that hydrochloric and nitric acids hinder or delay the formation of the yellow precipitate, and that molybdic acid solution and ammonium salts hasten or bring about its formation. Hydrochloric acid acts in the solution more energetically than nitric acid, and ammonium nitrate than ammonium chloride. The precipitate contains phosphoric acid and molybdic acid in the ratio, $1P_2O_5 : 24MoO_3$. In the precipitation of the phosphoric acid, the quantity of the free nitric acid must always be greater than is necessary, to preclude the possibility of a precipitate arising in absence of phosphoric acid, and a considerable quantity of ammonium nitrate can be dissolved in the solution in order to assist the separation of the precipitate.

A mixture is recommended of 37 c.c. of molybdic acid solution, 9 c.c. of nitric acid of sp. gr. 1·4, 62 c.c. of water, and 40 grams of ammonium nitrate. This remained clear for 24 hours. In such a mixture, to which 0·01 gram P_2O_5 was added, a very perceptible precipitate was formed, after 24 hours. Except in extraordinary cases, the precipitation may be effected within 12 hours, by (1) adding to the solution so much molybdic acid solution, that the latter is equal to four times the volume of the phosphoric solution, and at the most is decomposed by the phosphoric acid up to two-thirds of its quantity; and (2) by dissolving in the solution 25 grams of ammonium nitrate for every 100 c.c. of the mixed solution. A 20 per cent. ammonium nitrate solution is recommended for washing the precipitate, and in the first washings this must be mixed with $\frac{1}{30}$th of its volume of nitric acid, which prevents the separation of a difficultly soluble crystalline compound. The washing is complete when the filtrate is no longer immediately coloured by potassium ferrocyanide. After removing the greater part of the nitrate with water, the precipitate is removed from the filter to a weighed crucible, by washing. That adhering to the filter is dissolved off with warm dilute ammonia, concentrated by evaporation, treated with excess of nitric acid, and the solution quickly poured into the crucible. The whole is evaporated, and the ammonium nitrate driven off by gently heating over the wire gauze. The residue is hygroscopic, and must be quickly weighed after cooling in the exsiccator. The precipitate contains 3·794 per cent. of P_2O_5.

If arsenic acid be present, the precipitate is dissolved in excess of ammonia, and the solution is saturated with pure hydrogen sulphide (obtained from sodium sulphide), and warmed after addition of a solution of sulphur in ammonium sulphide. Precipitation is now effected with hydrochloric acid, and the filtrate is evaporated and again precipitated with molybdic acid.

For the estimation of phosphorus in iron, the powdered substance is treated with nitric acid, sp. gr. 1·4, and heated to complete decomposition; the solution is evaporated to dryness; the residue faintly ignited and dissolved in strong hydrochloric acid; and the phosphoric acid in the filtered solution is determined then in the manner above described. By following Korschell's prize method just as he describes it, it is possible that in an iron containing 0·1 per cent. of phosphorus, even the presence of the latter may not be detected. W. S.

Electrolytic Estimation of Cadmium. By E. J. Smith (*Deut. Chem. Ges. Ber.*, **11**, 2048—49).—The author finds that cadmium may be accurately estimated by the electrolytic decomposition of the *acetate* in aqueous solution (J. W. Clarke, *Ber.*, **11**, 1409). It is necessary to employ a current of medium strength, *e.g.*, two ordinary Bunsen's cells, and a solution of concentration about 1 : 50. The decomposition is complete in 3—4 hours. C. F. C.

Separation of Zinc from Nickel. By F. Beilstein (*Deut. Chem. Ges. Ber.*, **11**, 1715—1718).—The author describes a method for separating zinc and nickel, which consist first in making the solution of the nitrates or sulphates alkaline with ammonia, and then acidifying with citric acid. The zinc is removed completely from this solution by means of sulphuretted hydrogen. In the filtrate from the zinc sulphide, the nickel may, after treating with ammonia, be determined electrolytically. The author also points out that Brunner's method (*Jahres. f. Chemie.*, 1858, 621) fails in separating a small quantity of nickel from a large excess of zinc, the precipitation of the latter being incomplete.

In conclusion, the author makes the following observations:—1st. Caustic soda precipitates nickel completely from ammoniacal solutions; if, however, zinc be present the latter is also carried down. 2nd. Nickel and zinc may be completely separated by means of caustic soda and bromine; the first precipitate must, however, be dissolved and the operation repeated. 3rd. These two metals cannot be separated electrolytically, as the nickel always contain zinc. Finally, nickel may be completely precipitated electrolytically from a weak acid solution. P. P. B.

Further Note on Weil's Volumetric Method of Estimating Copper. By F. Weil (*Zeitschr. Anal. Chem.*, 1878, 438—440).—If a solution which contains copper is mixed with two and a half times its volume of pure hydrochloric acid, it shows on being boiled a yellowish-green colour: this is evident when the quantity of copper is too small to show a blue colour on addition of ammonia. The colour is at once destroyed by stannous chloride, and the disappearance of the colour in the boiling liquid serves as an indication of the end of the reaction.

The stannous chloride solution is titrated by adding it to a standard copper solution (·1 gram of copper in 10 c.c.).

The solution of the substance containing copper, after evaporation if necessary to expel nitric acid, is diluted to a known volume with water, a quantity taken which contains from ·05 to ·1 gram, mixed

with twice its volume of hydrochloric acid and then titrated. Oxidation by the air is prevented by the acid vapours evolved by boiling in the flask.

If antimonic acid is present, it is reduced with the copper, but on standing in a shallow dish for the night, the copper is reoxidised whereas the antimonious acid is not: hence the copper may then be titrated alone, and the antimony obtained by difference.

When hydrochloric acid is added in the above proportion, ferric salts can also be estimated directly by decolorisation on addition of sufficient stannous chloride. If copper and iron are present together, the two are titrated; the copper is then precipitated by zinc; and the iron oxidised by permanganate and titrated with stannous chloride, after addition of two and a half volumes of hydrochloric acid: copper and iron can thus be determined when together. This process is admirably suited for the estimation of copper, iron, and antimony in fahl-ores, arsenic acid not interfering. F. C.

Test for Arsenic. By O. Johnson (*Chem. News*, **38**, 301).—Place the mixture containing arsenious or arsenic compounds in a Marsh apparatus with a concentrated solution of potassic hydrate and a little aluminium wire. Upon warming, AsH_3 will be evolved, which may be subjected to the usual tests. If, however, the gas blackens silver nitrate, the proof is quite conclusive, since antimony by this process is not converted into SbH_3. The equations are :—

$$3H_3AsO_3 + 6Al + 18KHO = 3AsH_3 + 3Al_2(OK)_6 + 9H_2O$$
$$3H_3AsO_4 + 8Al + 24KHO = 3AsH_3 + 4Al_2(OK)_6 + 12H_2O.$$

D. B.

Volumetric Estimation of Manganese. By T. Morawski and J. Stingl (*J. pr. Chem.* [2], **18**, 96—101).—In the *J. pr. Chem.* [2], **18**, 90, and this volume, p. 206, the authors show that manganous chloride and potassium permanganate react so as to give the insoluble hydrated peroxide MnH_4O_8. It is easy to determine the proportions of this reaction volumetrically, but care must be taken that the hydrochloric acid set free in the reaction be kept so dilute that it cannot react on the precipitated hydrate. Into a measured quantity of manganous chloride solution, permanganate solution is dropped until at the edge of the solution a permanent rose-colour is observed. A temperature approaching that of boiling water is without effect upon the reaction. On determining volumetrically the hydrochloric acid in the filtrate from the hydrated peroxide, this was found (as it should) to represent chlorine close upon two-thirds of the chlorine in the manganous chloride. The reaction-equation (p. 206) shows that 1 mol. potassium permanganate, $K_4Mn_4O_{16}$, corresponds to 6 atoms of manganese, and also to 20 atoms of iron, as ferrous oxide. Thus the permanganate solution can be titrated with iron, and the value for manganese be derived; 10 atoms iron correspond with 3 atoms manganese. A volumetric method was now devised for determining the manganese in pig-iron, ferromanganese, &c. With high manganese percentage the results were usually 1 per cent. too high, but with 20 per cent. ferromanganeses good results were obtained. As the reaction does not proceed

well in presence of iron as chloride, this was removed by treatment with barium carbonate, and immediately after addition, the titration can be proceeded with without waiting for filtration. It is, however, better to filter, as then the end reaction can be observed more distinctly. The results show that, especially for the determination of small quantities of manganese, the method furnishes good results; with larger quantities of manganese the formation of a large quantity of precipitate renders the final reaction difficult to observe. W. S.

Modification of Bunsen's Method of Manganese Determination. By T. Morawski and J. Stingl (*J. pr. Chem.* [2], **18**, 101).—To prevent iodide solution being sucked back after the evolution of chlorine has ceased, a long narrow bent tube passes up the evolution tube, to within a few inches of the bend downwards into the bulb. It curves round sharply at the exit of the evolution tube, and runs up its outside (parallel to its other limb inside the tube), and finally makes its exit at the end of the stem of the inverted retort, where it bends downwards and is terminated with a piece of caoutchouc tubing closed by a pinch-cock. This is simply opened at the close of the chlorine evolution, whenever the symptons of receding on the part of the iodide solution make their appearance. W. S.

Simultaneous Determination of Carbon, Hydrogen, and Nitrogen in Elementary Analysis. By W. Hempel (*Zeits. f. Anal. Chem.*, 1878, 409—421).—The author burns the organic substance in a vacuum in a tube containing copper oxide and metallic copper; the resulting carbon dioxide is absorbed by soda-lime, and the water by calcium chloride, and the weights of the carbon and hydrogen are calculated from the increase of weight undergone by the absorption tubes. The nitrogen is collected in a measuring tube and its weight calculated from its measured volume.

The air-pump employed for removing the air before and nitrogen after the combustion, was one described by Töpler (*Dingl. polyt. J.*, **163**, 426). The toricellian vacuum is obtained by means of mercury. Full details of the construction and use of the pump are given at the beginning of this paper, with reference to accompanying diagrams.

The combustion tube is compactly filled in front with 5—8 cm. of copper powder; then follow 10—40 cm. of granular copper oxide, the mixture of substance with copper oxide, an asbestos plug and a platinum boat containing potassium chlorate: the end is drawn out as usual into a narrow oblique tube. No passage for the gases is made at the upper part of the tube.

The copper powder is prepared by heating copper oxide in a stream of hydrogen purified by passing through potassium permanganate solution: a litre of air is then passed through the glowing copper, the nitrogen of which complete removes the hydrogen from the copper powder. This powder yields no water when reoxidised, and completely decomposes nitrogen oxides even when the combustion commences in a vacuum.

When a liquid is to be burnt, the author introduces it in the usual way into a bulb which has two capillary tubes, one of these tubes

having been first closed by sucking into it a melted alloy of cadmium, lead, tin, and mercury (2 : 1 : 4 : 2 or 3): this hardens at once without bursting the tube: the other capillary is fused in the usual way. Since the above alloy fuses at 50—60°, the bulb, whilst remaining tightly closed at the ordinary temperature, can be opened during the combustion by gently heating the end of the capillary.

The absorption tubes contain little wads of cotton which prevent the gases from rushing too rapidly through the vacuous space at first, and thus escaping absorption. The calcium chloride tube also has a little bulb apparatus containing a few drops of sulphuric acid.

The process is commenced by exhausting the air from the combustion and absorption tubes: the potassium chlorate is then heated, and the oxygen which is evolved largely dilutes any traces of air which remain, and removes the air film from the surface of the copper powder. The whole is then once more exhausted, and the vacuum made perfect by heating the copper powder and thus absorbing the residue of oxygen. The combustion is then carried out as usual, heating only to dull redness: as soon as it is completed, the nitrogen is slowly drawn over into the measuring tube, giving time for the gas to find its way through the cotton wads. The narrow tube at the end of the combustion tube is afterwards broken, and oxygen drawn through to burn away any residual carbon, until the copper powder begins to oxidise: the gases are then removed into the absorption tubes by drawing in a stream of air. The process requires about the same time as that of Dumas; it is especially suited for the combustion of explosive substances which burn harmlessly under the diminished pressure.

The author gives results obtained by this process from aniline, picric acid, and nitroglycerin: the quantities employed were from one to four decigrams: the percentage errors were, for carbon −·3 to + ·5, for hydrogen + ·1 to + ·3, for nitrogen −·4 to + ·4. These numbers represent the greatest errors which were unaccounted for; theoretical numbers were frequently obtained. F. C.

Detection and Approximate Determination of Minute Quantities of Alcohol. By J. C. Thresh (*Chem. News.*, **38**, 251).—The author has devised a new method of detecting and estimating small quantities of alcohol, which is based on the fact, that traces of aldehyde, when boiled with caustic potash or soda and allowed to stand for a little while, exhibit a distinct yellow colour, or if 0·1 per cent. of aldehyde be present, a flocculent yellow precipitate is obtained.

The sample to be examined is distilled with oxidising agents—potassium dichromate being the most trustworthy—and the aldehyde formed is collected in caustic soda. To obviate the considerable bumping which takes place during the distillation and gives rise to unsatisfactory results, it is best to add a few pieces of pumice. The distillate is boiled for a few seconds, and allowed to stand for 2 hours. It is then compared with solutions containing definite quantities of aldehyde, and thus the amount of alcohol present in the sample ascertained. Potassium dichromate may also be used as standard. As, however, albumin, fibrin, gelatin, and lactic acid, yield traces of aldehyde when treated with potassium dichromate and sulphuric acid, it is necessary to remove

these compounds before applying the test. No substances besides these and the ethyl compounds are known to yield aldehyde when thus treated. D. B.

Detection of Chloroform. By E. Reichardt (*Arch. Pharm.*, [3], **13**, 252—254).—Although Fehling's solution is a very delicate test for minute quantities of chloroform, it cannot be applied to urine, as sugar also reacts with Fehling's solution. After administration of chloroform, therefore, the indigo test must be employed for the detection of sugar; this solution is decolorised by sugar and commercial dextrin, whereas pure dextrin and chloroform have no effect on it.

E. W. P.

Estimation of Hydrocyanic Acid in Bitter-almond Water. By H. C. Vielhaber (*Arch. Pharm.* [3], **13**, 408—410).—To the solution of hydrocyanic acid, magnesium hydrate suspended in water is added to alkaline reaction, and the solution titrated with decinormal silver solution, potassium dichromate being used as indicator. The magnesium hydrate has no action on the silver nitrate until all the chromic acid is precipitated. An addition of magnesium hydrate to all acid solutions in which potassium dichromate is used as indicator for silver nitrate is strongly recommended. E. W. P.

Test for Quinine. By O. Hesse (*Arch. Pharm.* [3], **13**, 490—495).—The apparatus employed is a test-tube 10—11 mm. in diameter and 120 mm. long. Near the centre are two marks, the lower of which marks off a volume of 5 cm. from the bottom, the upper being at such a distance from the lower mark as to include a volume of 1 c.c. 0·5 gram of the quinine to be tested is dissolved in 10 c.c. of water at 50—60°, cooled for ten minutes, and filtered into the "quininometer" up to the 5 c.c. mark; 1 c.c. of ether is added, and then 5 drops of ammonia; the tube is now corked and gently shaken. If after standing for a short time no crystals appear, the quinine may be considered as pure. The quinine may, however, not be absolutely pure, as the amount of ether will dissolve 0·25 per cent. of cinchonine, 0·5 per cent. of quinidine, and 1 per cent. of homocinchonidine and cinchonidine sulphates. If more of those substances are present, crystals will be observed in the ether. In the case of homocinchonidine or cinchonidine the crystals will be granular, but if cinchonine or quinidine be present the crystals will be concentrically grouped. Should as much as 3 per cent. of homocinchonidine or cinchonidine be present, the crystals will separate immediately, or at least within three minutes; but if ten minutes elapse before their appearance, then the percentage may be reckoned at 2; if only after twelve hours, then less than 1 per cent. is present. In the latter case some of the ether must be allowed to evaporate slowly. A crystalline residue shows the presence of 0·5 per cent. of these alkaloïds. Should the quinine sulphate contain 0·5 per cent. of cinchonine, or 1 per cent. of quinidine sulphates, these will also separate from the ether, but no account need be taken of these, as all commercial quinine contains these two alkaloïds. The above tests are intended only for druggists.

Quinine Hydrochloride.—The presence of cinchonine, cinchonidine, homocinchonidine, and quinidine hydrochlorides in quinine hydrochloride may be detected by treating 0·5 gram of the salt with 0·25 gram of crystallised sodium sulphate in 10 cm. of water at 60°, and then proceeding as detailed above. E. W. P.

Test for Quinidine. By O. Hesse (*Arch. Pharm.* [3], **13**, 495).—0·5 gram of quinidine sulphate and 0·5 gram of potassium iodide are dissolved in 10 cm. of water at 60°, then filtered after an hour, and to the filtrate is added a drop of ammonia. No cloudiness should result. E. W. P.

Behaviour of Potassium Thiocyanate with some of the Cinchona Alkaloïds. By O. Hesse (*Arch. Pharm.* [3], **13**, 481—490).—For the success of the experiments it is necessary (1) that the potassium thiocyanate be dissolved in an equal quantity of water; (2) that the sulphates of the alkaloïds be dissolved in water at 50—60° in the proportion of one part of sulphate to ten parts of water, and this solution be used after cooling and filtering; (3) that the observations be continued until all reaction ceases, which occurs generally in two minutes, seldom exceeding one hour. On the addition of potassium thiocyanate solution to quinine sulphate solution, stellar groupings of acicular crystals are formed, but this only occurs if the thiocyanate is in excess, as the quinine thiocyanate is more readily soluble in water than the sulphate. With cinchonidine sulphate the thiocyanate produces a milkiness, which finally resolves itself into concentrically grouped soft needles. Like quinine thiocyanate, cinchonidine thiocyanate may be completely precipitated from its solutions by excess of potassium thiocyanate. Homocinchonidine sulphate reacts with potassium thiocyanate like the cinchonidine salt, except that the change from the amorphous to the crystalline state is more rapid, and the crystals are also isolated as well as grouped. Quinidine thiocyanate crystallises in dendritic groups, with here and there long hexagonal plates. Potassium thiocyanate produces a white curdy precipitate with cold saturated solutions of cinchonine sulphate, whereas in dilute solutions prismatic and tabular crystals are formed. The tabular crystals are hexagonal and long, while the prisms are four-sided. Their appearances being microscopical, it is possible to detect the presence of one or more of these alkaloïds in a solution. A description of the phenomena observable when a definite amount of one alkaloïd is present in a solution of another is given as an example. E. W. P.

Estimation of the Alkaloïds in the Bolivian Cinchona Barks exhibited at the Horticultural Exhibition in Amsterdam. By W. Stoeder (*Arch. Pharm.* [3], **13**, 243—252).—25 grams of the air-dried barks were treated with 10 grams of calcium hydrate and 60 grams of water, and the resulting mass, after being perfectly dried, was exhausted with 92 per cent. alcohol containing 20 per cent. of chloroform, in a distillation displacement apparatus. After the operation was completed, which was generally in six hours, the alcohol in the quinine-lime mixture was displaced by water, and the alcoholic

fluid acidified with sulphuric acid, and the calcium sulphate thus precipitated was filtered off and washed with alcohol, leaving a yellow solution of the alkaloïds. This was concentrated, and then strongly acidified with sulphuric acid. Quinic acid and vegetable fats were then separated by filtration. The filtrate was concentrated and neutralised with ammonia. Before the point of neutralisation was reached, the sulphates crystallised out in the case of barks rich in quinine. These crystals were then filtered and dried, and consisted of quinine sulphate crystallising with 7 mols. of water. If then the quantity remaining in the mother-liquor, which amounts to $\frac{1}{760}$, be added to the weight of the above crystals, and the whole quantity multiplied by 0·289, we obtain the amount of quinine contained in the barks. After separation of the quinine sulphate, cinchonidine and quinidine were tested for, but as a rule they were present in very small quantities only. Lastly, the cinchonine and amorphous alkaloïds were precipitated from the mother-liquor of the quinine sulphate by excess of sodium hydrate. Addition of alcohol of 40 per cent. sufficed to separate the amorphous alkaloïds. The barks on an average contained 12 per cent. of water. The following is the result of the analyses:—

	Quinine.	Cinchonine.	Amorph. Alk.	Cinchonidine.	Total Alk.
Calisaya bark (monopol. quinine). (No longer to be obtained, the trees being destroyed)	3·1	0·49	0·195	—	3·795
Calisaya bark, from Yungas	4·268	0·496	0·164	—	4·828
Calisaya bark, with epidermis, from Yungas	1·724	0·468	0·192	—	2·364
Calisaya bark, from Inquisivi	3·292	0·772	0·272	—	4·336
Bark from Yurucares	—	1·288	0·236	—	1·524
Cascarilla Naranjada, from Prov. Larecuja	—	2·096	1·088	1·516	4·70
Bark from the twigs of the Naranjada	—	2·044	0·632	traces	2·676
Same, from Prov. Canpolican	—	·234	·036	—	0·27
Same, from Prov. Yungas	—	1·184	·652	—	1·836
Sample from Prov. Vallegrande	—	2·128	·408	—	2·536
False bark, called by Indians Car-hua Car-hua	0·308	0·76	·088	0·512	1·668

E. W. P.

Method for rapidly Incinerating Flour. By H. Borntträger (*Zeitschr. Anal. Chem.*, 1878, 440).—The ordinary method of incineration is tedious, but it can be completed in about twenty minutes by first mixing the weighed flour with an equal quantity of pure crystallised ammonium nitrate. The mixture is heated until it begins to smoulder, and the lamp is then removed until the combustion is finished; a few more crystals are strewn over the ash, which is then heated, at first carefully, and finally very strongly. Direct comparison

with the ordinary process of incineration without the nitrate, showed a difference of only one to five hundredths per cent. F. C.

Testing Beeswax for Rosin. By E. Schmitt (*Arch. Pharm.* [3], **13**, 212).—The adulteration of yellow beeswax with rosin is detected by boiling 5 grams of the wax with five times its weight of commercial nitric acid (sp. gr. 1·33) for one minute. It is then diluted with an equal volume of water, and saturated with ammonia. The alkaline liquid will be of a yellow colour if the wax be pure, but otherwise of a deep red-brown. 1 per cent. of colophony is easily detected by this process. E. W. P.

Technical Chemistry.

Iodine Industry in France. By C. Deite (*Dingl. polyt. J.*, **230**, 53—60).—About a year ago, Stanford (*ibid.*, **226**, 85) wrote a paper on the preparation of iodine, in which more especially the Scotch conditions were considered. It was shown how considerably the Chilian iodine obtained from the mother-liquors of the caliche of Peru competed with the Scotch industry, a circumstance which applies in a similar manner to the French conditions.

Of the 400 to 500 species of algæ found on the west coast of France only one dozen at the most are fit for the preparation of iodine. The following algæ are used: *Fucus vesiculosus*, *nodosus*, *siliquosus*, *serratus* (called "goëmous noirs" in France), *loreus* (lacets), *esculentus bulbosus* (tuet), *saccharinus* (frisou), *Digitatus stenolobus* (thali), and *Digitatus stenophyllus* (calcut). Each of these species grows at a certain depth of the sea; the deeper and slower it grows the more iodine will it contain. By taking the percentage of iodine in *Digitatus stenophyllus* as standard = 100, we obtain for *Digitatus stenolobus*:—

New leaf.	Stem.	Old leaf (goëmonds'avril).	Whole plant.
122·89	109·33	58·03	66·16

Saccharinus 45·48, *vesiculosus*, *nodosus*, *serratus*, *siliquosus* (goëmous noirs) as average 12·14, *esculentus* (*Alaria esculenta*) 10·84, and *bulbosus* 7·83.

The temperature seems to be of great importance to the assimilation of iodine, those species containing most which grow the furthest north. The percentage of iodine, therefore, will be at its maximum in winter, the minimum being in June, July, and August. The difference between the two seasons may amount to 40 per cent.

Saccharinus and *digitatus* grow at a depth of at least 5 to 11 meters below the lowest water mark at the time of ebb tide, and can be collected only at low water by means of boats specially constructed and fitted out. By the aid of rods 5 to 6 meters long, the ends of which are provided with sickles or hooks, the algæ are torn off, and then

rise to the surface. A squadron of 1,000 to 1,200 boats operates on the east coast of Finisterre. However, the circumstance that at the time of the lowest tides the sea is very rough, often hinders the collecting of deep-growing algæ; varec burners therefore generally take refuge to cut and floating algæ, these being procured with less difficulty. Cut algæ (goëmous decoupés) are those species which grow in very shallow water, whilst floating algæ (goëmous épaves) are those which are driven to the coast by storms, &c. The latter often reach the coast after they have been driven about in the sea for several days. This may considerably alter their consistency without materially changing their outer appearance. (Algæ which had been floating in the sea for two days contained only 59 per cent. of their original contents of iodine, while after ten days' delay they only showed 7 per cent. of their original iodine.) Most species are annual plants; *Digitatus stenophyllus*, however, is perennial, a circumstance which undoubtedly explains its large percentage of iodine.

As to the preparation of iodine in France, the author mentions that, with the exception of one firm, the algæ are to the present day worked up in the most primitive manner; the burning is still undertaken in open pits, the objection to this being the drying of the weeds previous to the burning, whereby much loss of iodine is occasioned. A better process is that adopted by Pellieux and Mazé Launay, who abandon the use of the ordinary cut and floating algæ, and work up those species which are collected by means of boats specially adapted to the purpose. The algæ are burnt without being dried. Terrace-like elevations are erected in the works, which consist of three breaks. In the first place the algæ are spread out on the top surface in layers, and allowed to drain for four to five hours, after which they are transferred to the next lower surface. Here they are allowed to ferment for 48 hours, whence they are brought to the lowest surface. They are now prepared sufficiently for further treatment. The juice which is obtained from the second and third layers is collected. It shows a strength of 7° to 8° B., and is richer in iodine than the algæ. (22,000 t. of juice give 1 t. of salt (salin), containing 20·2 k. iodine.) It is evaporated to 32° B., and then burnt in calcining furnaces together with the algæ. (12·6 t. algæ yield on an average 1 t. soda, containing 10·5 k. iodine.)

The varec obtained in this manner is lixiviated, the liquors being evaporated to 35° B., and calcined. Thus all alkaline sulphides or thiosulphates are decomposed. The calcined mass is again lixiviated, the first liquors containing the potassium and sodium iodides. The residual salt, after removal of all iodine, is dried and sold as manure. The mother-liquors are evaporated and calcined, a white salt resulting, which contains 30 to 35 per cent. of iodine. By lixiviating this with cold water, &c., a salt may be obtained consisting of 72·4 KI and 27·6 NaI. D. B.

Extraction of Sulphur by means of Superheated Steam. By G. T. Gerlach (*Dingl. polyt. J.*, **230**, 61—67).—This method consists in volatilising and distilling sulphur ores by heating them in iron or clay retorts to the melting point of sulphur, or to a slightly higher

temperature, and passing superheated steam into the hot mass. The distillation proceeds with great rapidity, whilst without steam the vapours of sulphur distil over very slowly, and require a high temperature. The process is especially suitable for the recovery of the sulphur from "gas purification residues," since the extraction of the sulphur by means of carbon bisulphide seems to be attended with much difficulty. As a novelty the author claims the use of superheated steam, obtained by passing vapour of water through a red-hot tube, as the distillation of sulphur by means of steam of a pressure of 3 to 3·5 atmospheres has been known for some time. D. B.

Metallurgy of Nickel and Cobalt. By W. A. Dixon (*Chem. News.* **38**, 268—270).—The author undertook this research with a view to improvements in the extraction of nickel and cobalt from the ores. The sources of nickel, previous to the discovery of the New Caledonian deposits, consisted chiefly of speiss, the residue from the manufacture of smalt, which contains from 6 to 8 per cent. of nickel and 3 per cent. of cobalt, and a few pyrites ores containing copper and nickel. To extract the metal from the ores, the speiss is fused with fluorspar and chalk, to remove part of the iron and obtain an enriched matt. This matt is ground, thoroughly roasted, to expel arsenic and sulphur, and convert the metals into oxides, which are then dissolved in hydrochloric acid. The solution is diluted, any ferrous chloride converted into ferric chloride, and the latter precipitated by milk of lime, any arsenic being removed simultaneously. The copper in the filtrate is then converted into the sulphide, and from the clear solution cobalt is precipitated by calcium hypochlorite, and afterwards the nickel by milk of lime.

The author found that although the nickel could not be separated from the silicate, it was nevertheless possible to separate nickel oxide from iron oxide by treatment with gaseous hydrochloric acid. The New Caledonian ore is very infusible, from the large proportion of magnesia it contains, and some cheap flux containing other silicates was necessary to obtain the nickel in a metallic or reguline state. Copper ore furnace-slag with half its weight of ore yielded a sufficiently fusible charge. The following table gives the complete analysis of calcined speiss, containing oxides of nickel, cobalt, copper, zinc, iron, and arsenic:—

I. Treated with gaseous HCl gives—

Distillate.	Residue II.
Containing Zn and As.	Containing Fe_2O_3, Cu_2Cl_2, $FeCl_2$, $NiCl_2$, $COCl_2$, with traces of Ni and Co.

II. Treated with hot water gives—

Residue III.	Solution A.
Containing Fe_2O_3CuCl. Traces of Ni.Co.	Containing $FeCl_2$, $NiCl_2$, and $CoCl_2$.

A. Treated with brine gives—

Residue.	Solution.
Other metals returned to melting furnace.	Containing CuCl, from which Cu is precipitated by iron.

III. Treated with Cl until all $FeCl_2$ is converted into Fe_2Cl_6, and then boiled with NiO—

Precipitate.	Solution IV.
Fe_2O_3 and ferric oxychloride, with the excess of NiO returned to roasting furnace.	Containing $NiCl_2$ and $CoCl_2$.

IV. Treated with Cl in presence of NiO—

Precipitate.		Solution.	
CoO and excess of NiO added. Treated with dilute HCl.		Pure $NiCl_2$ evaporated to dryness, and ignited in current of steam.	
Residue.	Solution.	Gas.	Residue.
CoO.	$NiCl_2$.	HCl returned to I.	NiO to reducing furnace.

D. B.

Purification of Cast-iron from Phosphorus. By S. Kern (*Chem. News*, **38**, 301).—The author has repeated William's process for purifying cast-iron from phosphorus, the results being very satisfactory. The process is based on the following operation:—Fluid pig-iron is poured into a crucible containing mill-scale in a fluid state, with an addition of about 20 per cent. of pure sand. The contents are then shaken for about a quarter of a minute, and then the refined metal is poured into moulds. Care must be taken not to overheat the metal. D. B.

Distribution of Manganese in Ferro-Manganese Alloys. By S. Kern (*Chem. News*, **38**, 268).—Since it has been remarked that the manganese in ferro-manganese alloys is often very unequally distributed throughout the mass, the author thought it interesting to undertake some experiments in this direction. A piece of ferro-manganese weighing 1,500 grams was provided for this purpose, six samples from different parts being analysed. The manganese was estimated as mangano-manganic oxide, according to Eggert's method. The results are:—

	A.	B.	C.	D.	E.	F.
Si.....	0·20	0·19	0·20	0·20	0·20	0·19
S	0·02	0·02	0·01	0·02	0·02	0·01
P	0·08	0·07	0·07	0·07	0·08	0·07
Mn	45·60	47·10	46·80	45·46	44·90	46·70
C	5·70	5·81	6·01	5·90	5·95	5·98

D. B.

Chrome Steel. By Boussingault (*Ann. Chim. Phys.* [5], **15**, 91—126).—The attention of metallurgists has for some years past been directed to the fact that chromium has the property of communicating to steel a homogeneous structure, fine grain, and remarkable smoothness of fracture—qualities which are desirable for many purposes. Chrome-steel is manufactured in the United States by a patented process, which consists in adding to ordinary steel definite quantities of an alloy of chromium and iron of known composition. This alloy (ferrochrome) is obtained by fusing in plumbago crucibles a mixture of chrome ironstone with 6 or 8 per cent. of charcoal or

anthracite, and a flux composed of calcium or sodium fluoride and lime, or of borax and sodium carbonate, according to the nature of the earthy impurities in the mineral. In some cases cast-iron containing as much as 7 per cent. of chromium is obtained directly in the blast-furnace. Ferrochrome, chrome-steel, and cast-iron containing chromium, are thus manufactured in the United States under patents taken out without regard to what had been previously done. In point of fact cast-iron containing chromium was made in Central America as long ago as 1866, long before it was patented in the United States.

The discovery of chrome-steel and ferrochrome is due to Berthier, who published a memoir on the subject in 1820 (*Ann. Chim. Phys.* [2], **17**). He made chrome-steel by fusing cast-steel with an alloy of iron and chromium obtained by reducing the mixed oxides of these metals. Two specimens of the metal, containing respectively 1 and 1·5 per cent. of chromium were found to forge perfectly, and to be well adapted for making cutlery.

The author has proved experimentally that chromium alone does not give to iron either increased hardness or greater elasticity after tempering. Chromium, therefore, cannot be used as a substitute for carbon, as claimed by one patentee.

The manufacture of ferrochrome and chrome-steel was introduced into France in 1875. The following observations refer to French products.

Ferrochrome, as obtained by the reduction of chrome ironstone in presence of a flux, varies considerably in properties according to the proportions of carbon and chromium it contains. An alloy containing 15 per cent. of chromium is hard and tough; its fracture is slightly lamellar, white, and silky by reflected light. With 25 to 30 per cent. of chromium the alloy is white and brilliant, and exhibits needles disseminated throughout its mass. As the proportion of chromium increases these needles become smaller, and the alloy more brittle. An alloy containing 68 per cent. of chromium is hardly fusible in a wind-furnace.

These statements refer to alloys saturated with carbon. In alloys containing less carbon the needles appear only with a higher proportion of chromium, and the fracture is less white. As the proportion of carbon increases the brilliant white needles are seen in the fracture to become more and more numerous.

Chrome-steel.—The addition of chromium to steel confers upon it a high degree of elasticity, which is in some cases almost double that of ordinary steel. At the same time the breaking strain of the metal and its resistance to blows are greatly increased.

Chrome-steel is, however, more difficult to work than ordinary steel containing the same proportion of carbon. Untempered steels containing 2 to 4 per cent. of chromium and 1·2 to 1·4 per cent. of carbon, are so hard as to be drilled with difficulty with the steel drills in ordinary use. After tempering at a cherry-red heat in water chrome-steel exhibits an extraordinarily fine grain; with a high proportion of chromium and of carbon the fracture becomes almost vitreous. The same metal tempered at a higher temperature acquires a fine grain, resembling that of porcelain.

The crystalline structure of ordinary steel is rendered finer by the addition of chromium, and it is to its fineness of grain that the superior tenacity exhibited by chrome-steel under all circumstances appears to be due. J. R.

Keith's Process for Desilvering and Refining Raw Lead by Electrolysis (*Dingl. polyt. J.*, **230**, 75).—This process has been tried practically on a small scale, and gives satisfactory results. Its theoretical basis is indisputable, if we disregard the one point, viz., that zinc is present in raw lead. The former is still more electro-positive than the latter, it will therefore be deposited at the cathode with the lead. Although the behaviour of several metals alters in accordance with the solutions in which they are treated, *e.g.*, silver, antimony, and copper, can show themselves, especially in alkaline solutions, more electro-positive than lead, this does not hold good with zinc and lead. According to Faraday, the electro-chemical series for hydrochloric acid is, antimony, silver, nickel, bismuth, copper, iron, lead, tin, cadmium, and zinc. Keith prefers the use of a bath of acetic acid to hydrochloric acid, more for the sake of conduction and attack than to produce any change in the electro-chemical position of the metals. His process is very clean and simple, bye-products are not obtained, whilst the desilvering and refining operation is very perfect.

D. B.

Extraction of Gold, Silver, and other Metals from Pyrites. By W. A. Dixon (*Chem. News*, **38**, 281—283; 293—294; 301—303; and **39**, 7—8).—Since the extraction of gold from complex minerals is a subject well worthy of investigation, the author undertook a complete series of experiments with a view of obtaining a ready method of separating this substance from pyrites.

An ore from Mariner's Reef, Gympie, was worked on, which in the rough yielded on analysis Cu = 6·2; Pb = 0·19 (Au = 3 ozs. 3 dwts., 3 grs. per ton; Ag = 32 ozs. 9 dwts. 3 grs. per ton). Another larger portion from the same reef, after being ground and washed so as to remove as much as possible of the quartz, which was found to amount to about 60 per cent. of the rough mineral, gave—

Cu.	Pb.	Sb.	Au and Ag.	Fe.	S.	Si.	As and loss.	
17·02	2·01	3·90	0·22	31·41	37·86	7·16	0·42	= 100·00

Gold = 12 ozs. 10 dwts. per ton; silver 62 ozs. 9 dwts. 16 grs. per ton. The author had also a small lot of copper pyrites from the same place, containing 24 per cent. Cu, and gold equal to 78 ozs. 8 dwts., and silver 4 ozs. 2 dwts. 10 grs. per ton; arsenical pyrites, containing when thoroughly roasted 11 ozs. 18 dwts. per ton; iron pyrites, containing when roasted 5 oz. 6 dwts. 3 grs. per ton.

A large number of experiments was undertaken, the mercury, chlorine, and potassium cyanide methods giving unsatisfactory results. It is shown that no method exists by which the precious metals can be removed and the base metals left, and it was therefore necessary to remove the base metals at the earliest stage possible, and leave the precious metals as a residue. After a whole series of smelting

trials the following experiment was made, which opened a prospect of the attainment of the desired result. By calcining the pyrites, and mixing the residue with raw ore and again calcining, then adding raw ore and continuing the operation, it was noticed that after each addition of pyrites considerable quantities of white vapours were evolved, arising from the formation of sulphuric anhydride. The amount of the latter was determined, and it was found that by proper management nearly three-fourths of the sulphur present in the ore could be obtained as sulphuric acid, either in the free state or in combination with copper and iron. As it was probable that such a result would not be obtained on a large scale, the author proceeded to examine the action of aqueous sulphurous acid, and found that by treating ore calcined at a low temperature therewith, a considerable quantity of iron sulphate was obtained in solution along with the copper sulphate; also that, as observed by Muspratt, aqueous sulphurous acid readily attacks finely divided metallic iron, forming sulphite and thiosulphate. It was therefore necessary to calcine the ore at a low temperature, and extract the copper and iron sulphates formed with the mixed sulphurous and sulphuric acids formed during the roasting, then to reduce all the iron to the metallic state, and remove it in the same manner, when the gold, silver, antimony, and lead, would be left. The points to be decided were, how to reduce the iron to the metallic state, and to obtain the copper from solution. The reduction of the iron is necessary, because the sulphuric acid obtained is too dilute to act on the ferric oxide, and the quantity would be insufficient to form ferric sulphate, whilst sulphurous acid has no action on the ferric oxide. Although hydrogen and coal-gas reduce iron readily, the former could not be used on account of the danger of explosion and the cost, while the latter deposited at a low temperature much finely divided carbon amongst the iron, which rendered melting it difficult, and the powder was very pyrophoric. The author, however, found that reduction by finely-ground carbon at a low red heat could be so managed as to obtain the iron as a metallic powder, which was readily attacked. For the removal of the copper from solution the author tried crystallisation, and the result of many trials showed that by taking a cold saturated solution of copper sulphate, adding sulphuric acid, and saturating with sulphurous acid, a solution was obtained which would render all but traces of the copper and sulphate of iron in well-roasted pyrites soluble without actually dissolving any. It deposited crystals on being mixed with the calcined ore in consequence of the copper and iron sulphates withdrawing crystallisation-water. By then washing by displacement with a boiling hot solution of copper sulphate previously saturated in the cold, as long as the escaping solution deposited crystals on cooling, the residue was obtained saturated with a solution of copper sulphate, which would not deposit crystals. This solution could be so displaced by water equal to one-half the bulk of the residue as to leave only 0·67 per cent. copper in a soluble form, whilst if an equal bulk of water was used the copper left was only 0·12 per cent.

In conclusion the author describes the complete method of separating 12 lbs. of the dressed pyrites, of which an analysis is given

above. The method of treatment of the concentrated ore or regulus, is the same, whether the sulphides are rich in the precious metals or not, but requires variation according to—first, the presence or absence of copper; second, the proportion of copper; and third, the presence or absence of lead. Details of the plant required, and the mode of working up the pyrites on a large scale are given. D. B.

Desirability of fixing by Analysis some Standards of Value for Beer, based on the Qualities usually sold in Large Towns. By C. Estcourt (*Analyst*, 1878, 325).—The author believes that it is not merely desirable, but absolutely necessary, that some definite standards both of strength and composition should be recognised for beer sold in the ordinary manner by retail.

As only three qualities of beer are recognised by the general public in the large towns in England, the author thinks that it would be quite possible, without seriously restricting the freedom of trade, to enact that these three qualities should be (within certain limits) of certain definite original gravities.

The table appended to the original paper shows that, although the mineral matter in some cases decreases or increases in quantity as the beer is of a lower or a higher gravity, still this rule does not always hold good; and it is found that a beer having an original gravity of 1066·4 has more mineral matter per gallon (excluding sodium chloride) than the beer of 1069 original gravity. This serious irregularity prevents our estimating the value of a beer, or its freedom from added water, by the ash alone. It is to the use of varying quantities of sugar with the malt in brewing that these irregularities in the quantity of mineral matter in a beer are due. However, a low ash is fairly good evidence that a beer is not entirely made from malt.

The author has tried several methods for making an accurate determination of the value of a beer by analysis. The data required are:—The original gravity (which also gives in the sp. gr. of the extract the percentage of solid matter), the total ash, the sodium chloride, the phosphoric acid, and the ammonia produced when the beer is Wanklynised. The phosphoric acid found and the ammonia produced by Wanklyn's permanganate process will fairly indicate the malt used, and the ash will show within certain limits the amount of sugar used. In any beer analysis, it is obvious that a knowledge of the water used in brewing is absolutely necessary.

Regarding the use of bitters other than hops, the author points out that the Government specifically refused to define beer as malt and hops when asked to do so three years ago. To obtain such a change, it is necessary that not only the public analyst, but the general public, should work, and then, and not till then, will a satisfactory result be arrived at.

A table giving the complete analysis of eight samples of beer is appended to the paper. D. B.

Clarifying and Preserving Wine. By L. Weigert (*Chem. Centr.*, 1878, 702—703).—Kaolin and Spanish earth are recommended for clearing wine; the finest particles of these silicates are decom-

posed by the acids of the wine, with precipitation of gelatinous silica, which carries down with it those substances which, when held in suspension, render wine turbid. The amount of free acid is diminished by the use of those materials, Spanish earth exerting a greater action in this respect than kaolin.

Little or no change is produced in the colour of wine by the use of those silicates; a somewhat milder taste is imparted to the wine after clarification.

Kaolin and similar silicates remove certain nitrogenous bodies from wine, and thus a wine clarified by their use may be kept for a considerable time exposed to air without undergoing fermentative changes; those silicates, therefore, may be said to act as preservatives of wine.

The presence of a very small quantity of free acid in a wine suffices to decompose portions of kaolin added. If wines be very poor in alcohol, clarification by kaolin is not advisable; 1 per cent. of kaolin, calculated on the weight of wine, is the maximum that should be employed under any circumstances, whilst from one-third to one-half less of Spanish earth is sufficient. Temperature has little influence upon the process of clarification. From four to six weeks are required to render the wine perfectly clear. M. M. P. M.

Manufacture of Resorcin, Eosin, and other Derivatives of Resorcin. By Bindschedler and Busch (*Chem. News*, **38**, 226).—The authors give an account of the recent improvements in the manufacture of these colours.

1. *Resorcin.*—90 kilos. of fuming sulphuric acid of 80° B. are poured into a cast-iron pot fitted with agitator and leaden cohobator. 24 kilos. of pure benzene are added gradually. The vapours are condensed in the cohobator and fall back into the pot. After three hours' agitation the reaction ceases, when the cohobator is removed, the cover of the pot being connected with a distillation worm. The contents are heated gradually to 275°, the benzene-sulphonic acid formed in the first instance being converted into the disulphonic acid. The whole is kept at this temperature for about twenty minutes. The mass is then cooled, boiled out with water limed until neutral, filter-pressed, and the filtrate is treated with sodium carbonate. The mixture is filtered, and the effluent liquid evaporated to dryness. 60 kilos. of this product are heated in a cast-iron boiler with 150 kilos. of caustic soda of 76° B. for eight to nine hours at 270° with constant agitation. The heated mass is dissolved in hot water, and hydrochloric acid added to the hot solution to slight acid reaction, the liquid depositing a small quantity of tarry matter. When cold the whole is filtered and introduced into an extraction apparatus, consisting of large copper cylinders of 150 liters' capacity. These are entirely filled with the liquid to be extracted, and a current of ethyl ether is passed through them very slowly. The ether in its passage becomes saturated with resorcin, and is received in stills, where it is distilled as it enters. The residue in the still solidifies on cooling to a crystalline mass, which is heated in enamelled vessels to 215° to expel the last traces of ether and water. The mass obtained forms the commercial product contain-

ing 92 to 94 per cent. of resorcin, the impurities being phenol and tarry matter. According to this method the yield obtained is almost theoretical.

2. *Fluoresceïn* is obtained by fusing 100 parts of resorcin with 75 parts of phthalic anhydride at 210° for an hour. The mass is cooled and ground finely. Purification is not needed.

3. *Yellowish eosin* soluble in water. 1 kilo. of fluoresceïn is ground finely and treated with 10 liters of alcohol, 1·1 kilos. of bromine being added very slowly, with constant stirring. All the fluoresceïn, which is already partially bromised, is now in solution. A further portion of 1·1 kilos. of bromine is added, each drop forming a crystalline precipitate of tetrabromo-fluoresceïn. After decantation, the crystalline deposit is washed with a little alcohol, then with water until completely neutral. It is now stirred up in hot water, and carefully saturated with soda, care being taken not to render the liquid alkaline: in this way the soda salt of tetrabromo-fluoresceïn is obtained.

4. *Bluish eosin* soluble in water. To prepare the soda salt of tetraiodo-fluoresceïn, fluoresceïn is dissolved in alkaline water, the proportionate quantity of iodine added, previously dissolved in caustic soda. By the addition of an acid a crystalline precipitate is obtained, which, when dissolved in dilute soda and evaporated, forms the commercial product.

5. *Safrosin* soluble in water. 9 kilos. of tetrabromofluoresceïn are dissolved in alkaline water, and 8 kilos. of sodium nitrate added. The mixture is heated to boiling, and 15 kilos. of 66° B. sulphuric acid are added. The precipitate is filtered off, washed, dissolved in dilute caustic soda, and evaporated. The salt obtained dyes wool with a more bluish-red tinge than tetrabromofluoresceïn.

6. *Eosin* soluble in alcohol. This substance yields shades which are more solid than those obtained from eosin soluble in water, the methylic derivative having a more yellowish tone than the ethylic. 5 kilos. of tetrabromofluoresceïn are mixed with 10 liters of pure methylic alcohol and 9 kilos. of 66° B. sulphuric acid, and heated on the water-bath for four hours. The mixture is poured into water, filtered, washed, and the precipitate treated with potash. The mass when dried dissolves readily in a mixture of equal parts of water and alcohol, the solution displaying a splendid fluorescence.

7. *Resorcin blue* is a new derivative of resorcin, finely dichroic, which gives on silks a reddish-blue shade, beautifully fluorescent.

D. B.

Testing Lubricating Oils. By C. Deite (*Chem. Centr.*, 1878, 558).—The method consists in placing equal quantities of the various oils on an iron plate, and judging of their relative values by their fluidity as determined by the rate at which they spread over the plate.

M. M. P. M.

General and Physical Chemistry.

Electro-chemical Actions under Pressure. By A. Bouvet (*Compt. rend.*, **87**, 1068—1070).—The author has made a series of experiments on the decomposition of water by electricity when the products are confined so as to exercise a pressure equal to that of several hundred atmospheres. He finds that the amount of water decomposed, and the quantity of electricity required for that purpose, are independent of the pressure, also that the temperature remains sensibly constant. The results are in perfect accordance with the theoretical formula for the work done in compressing the gases. Oxygen and hydrogen are liberated with equal facility, and may be collected together or separately. Contrary to the received view, there was in all cases an absence of any secondary phenomena indicating a re-combination, the manometer for hours indicating a perfectly regular increase of pressure, minute by minute. There was no danger of detonation when the gases were collected in one vessel, even when the pressure was considerable, as care was taken to keep the electrodes, which were of platinum, completely immersed in the liquid.

R. R.

Spectrometric Determination of High Temperatures. By A. Crova (*Compt. rend.*, **87**, 979—981).—From theoretical considerations discussed by the author in previous papers (*ibid.*, **87**, 322, *Jour. de Phys.*, November 7, 1878) he has derived a purely optical method for the determination of high temperatures. The law forming the basis of his method is that "two incandescent bodies having the same power of radiation are of the same temperature when the intensities of all simple radiations of their continuous spectra bear a constant ratio to each other; that is to say, are equal to each other when the more intense has been weakened (by means of two nicols), so as to make the intensities of any two radiations, of the same wave-length, in the two spectra in question equal."

The method consists in measuring, by means of a spectrophotometer, the ratio of two determinations (λ and λ' of different wave-lengths) from two incandescent sources, one of a known temperature T, the other unknown, x; then $\frac{I}{I'}$ and $\frac{i}{i'}$ represent these ratios, and their quotient the ratio of the intensities of the radiation λ' in the two spectra, when the more intense has been weakened, so as to give the same intensity as the radiation λ in the two spectra.

The author has constructed an arbitrary scale, the fixed wave-lengths being 676 and 523.

This method has the advantage that the scale of temperatures may be extended beyond those which can be measured by an air thermometer, and it can also be used to determine the temperature of bodies at a distance, such as the sun, stars, &c. L. T. O'S.

Specific Heat, and Latent Heat of Fusion of Palladium. By J. Violle (*Compt. rend.*, **87**, 981—984).—The method employed for the determination of the specific heat of platinum between 0° and 1,200° (*ibid.*, **84**, 543—546) was adopted for the determination of the specific heat of palladium between 0° and 1,300°. The author gives a table of results obtained, and compares them with the numbers calculated from the formula (1) $C_0^T = 0{\cdot}0582 + 0{\cdot}000010T$. The true specific heat at T°, $\frac{dQ}{dT}$ is equal to (2) $\gamma_T = 0{\cdot}0582 + {\cdot}000020T$, from which $\gamma_0 = 0{\cdot}0582$, $\gamma_{500} = 0{\cdot}0682$, $\gamma_{1000} = 0{\cdot}0782$, $\gamma_{1300} = 0{\cdot}0842$.

The temperature of fusion of palladium has been determined:—

(1.) By heating a solid piece of palladium as near to the melting point as possible, plunging it into a calorimeter, and calculating the temperature to which the metal has been heated from the specific heat given by formula (1).

(2.) By heating a mass of platinum by the side of a mass of palladium and obtaining two temperatures very near to each other, such that at one the palladium melts, but not at the other, these temperatures being in each case determined by means of the platinum, by the calorimetric method. By these methods the temperature of fusion of palladium is found to be 1,500°. It is noteworthy that palladium, like platinum, softens before it melts, so that it can be welded at a temperature somewhat below 1,500°. The total heat of fusion according to the mean of three experiments is 146·1 th. units for 1 gram of palladium, and by deducting 109·8 th. units, the quantity of heat necessary to raise 1 gram of palladium from 0° to 1,500°, the latent heat of fusion of palladium, is found to be 36·3 th. units. L. T. O'S.

Gas Regulator for Air-baths. By L. Cresti (*Gazzetta chimica italiana*, **8**, 292—294).—This regulator somewhat resembles Bunsen's, but the air-chamber of the instrument alone is inside the air-bath, and communicates with the part containing the mercury by means of a tube. As the air expands, the pressure causes the mercury to rise and partly closes the tube by which the gas enters. It has the advantage over Bunsen's regulator that the mercury has not to be heated, and therefore it is more sensitive, but it has the same defect of being affected by barometric changes; this is avoided in Page's regulator (this Journal, 1876, **1**, 24). C. E. G.

Process for Determining the Vapour-densities of Substances which attack Mercury, or which boil above 440°. By V. and C. Meyer (*Deut. Chem. Ges. Ber.*, **11**, 2253—2260).—This is an improvement of V. Meyer's method (*Ber.*, **11**, 1868, this Journal, 1879, 177) for determining vapour-densities by measuring the volume of air expelled by the vapour of a known weight of substance. The original paper must be consulted for the details of the process. W. C. W.

Density and Coefficient of Expansion of Liquid Methyl Chloride. By C. Vincent and Delachanal (*Compt. rend.*, **87**, 987—989).—The method employed in the determination of the coefficient of

expansion of liquid methyl chloride was the same as that employed by Pierre in his determinations of the coefficient of expansion of organic liquids. The apparatus consisted of a thermometer with a bulb 2·2 c.c. capacity, and a tube 70 cm. long calibrated, and containing the methyl chloride; between −25° and +45° the liquid expanded so as to fill nearly the whole length of the tube. The volume of the bulb up to the first mark at 0° was 2·23478 c.c., and that of each division 0·00002687 c.c.; the weight of methyl chloride 2·2 grams. From these data, the authors have determined the sp. gr. of the liquid between the temperatures 30° and 50°, of which they give a table, and from which have constructed a curve, and also the coefficient of expansions for the temperatures 13·4°, 23·8°, and 39°, at which temperatures the volumes = 1·02657, 1·04862, and 1·08470 respectively, the volume at 0° = 1. From these numbers the results obtained according to the formula $V_t = V_0(1 + \alpha t + \beta t^2 + \gamma t^3)$ are $\alpha = 0{\cdot}00193929$, $\beta = 0{\cdot}00000183121$, and $\gamma = 0{\cdot}000000105916$. L. T. O'S.

Specific Gravity Determinations. By F. W. Clarke (*Deut. Chem. Ges. Ber.*, **11**, 1504—1507).—The author has determined the specific gravities of the following compounds:—

	Sp. gr.	t°.
$HgCy_2$	4·0262	12°
$HgCy_2HgO$	4·437	19·2°
$HgCy_2HgCl_2$	4·531	21·7°
$HgCy_2 2KCy$	2·447	21·2°
$HgBr_2$	5·7461	18°
KBr	2·712	12·7°
$HgBr_2.KBr$	4·412	17·2°
$HgBr_2.KBr.H_2O$	3·865	20—24°
$(NH_4)_2Cr_2O_7HgCl_2.H_2O$	3·329	21°
HgI_2	6·231	10—19°
$2(KI.HgI_2)3H_2O$	4·289	23·5°
Cobalt formate + $2H_2O$	2·1286	22°
Nickel „ + $2H_2O$	2·1547	20·2°
$N(CH_3)_4I$	1·827	17°
$N(CH_3)_4I.HgI_2$	3·968	24°
$CdCl_2$	3·938	23°
$CdCl_2.2H_2O$	3·339	18·2°
$2CdCl_2.SrCl_2 7H_2O$	2·718	24°
$2CdCl_2.BaCl_2 4H_2O$	2·952	24·5°
$PtCl_2.2KCl$	3·2909	21°
$H_2TeO_4.2H_2O$	2·999	25·5°
H_2TeO_4	3·425	18·8°
$(NH_4)_2TeO_4$	3·024	24·5°
Thallium tellurate dried at 180°	6·742	16°
Cobalt acetate + $4H_2O$	1·7031	15·7°
Nickel „ + $4H_2O$	1·7443	15·7°

The molecular volume and specific gravity of the following salts have been calculated from the results of numerous determinations.

There is a constant difference in the molecular volume of 16·5 for each CH_2 group :—

	Molec. vol.	Sp. gr. of 16·5 calculated.
Barium methylsulphate	176	2·244
,, ethyl ,, ...	209	2·024
,, propyl ,, ...	242	1·863
,, isobutyl ,, ...	275	1·780
,, amyl ,, ...	308	1·646

	Molec. vol.	Sp. gr.
Potassium methyldisulphocarbonate	88	1·658
Ethyl salt	104·5	1·531
Isobutyl salt	137·5	1·367

W. C. W.

Reciprocal Displacements between Oxygen, Sulphur, and the Halogens, when combined with Hydrogen. By Berthelot (*Compt. rend.*, **87**, 667—671).—It has been already shown that when any two of the above elements, entering separately into combination with a third, evolve different amounts of heat, the element which evolves the greatest amount of heat will, under suitable conditions, displace the other from its combination with the third. Chlorine, therefore, displaces bromine and iodine, and bromine displaces iodine, both in the gaseous hydracids and in their aqueous solutions. In like manner chlorine and bromine ought to displace sulphur from hydrogen sulphide, both in the gaseous state and in solution; but although iodine should displace sulphur in dissolved hydrogen sulphide, sulphur, on the contrary, should decompose hydriodic acid gas, with formation of gaseous sulphuretted hydrogen, since the union of hydrogen and sulphur to form gaseous H_2S evolves + 3·6 units of heat, whilst 0·8 unit is absorbed in the formation of hydriodic acid gas. The author has made new experiments upon this point.

Dry hydrogen sulphide was enclosed with a little iodine in a sealed tube, and heated to 500°, but no reaction took place. On the other hand, dry hydrogen iodide and sulphur in a similar arrangement reacted immediately, even in the cold, and on heating to 100° the reaction was complete. When the tube was opened under water, the rising of the latter showed a diminution of nearly one-half the volume of the gaseous contents of the tube; the inverse action then immediately sets in, and the hydrogen sulphide is decomposed in its turn by the sulphur iodide formed, reproducing sulphur and solution of hydriodic acid. These two inverted actions can be effected, even in presence of water, with a solution containing more than 52 per cent. of hydracid; if iodine be dissolved in it and hydrogen sulphide passed into the solution, no ultimate reaction is observable, because the liberated sulphur attacks and destroys the hydrogen iodide as fast as the latter is formed.

Oxygen should and does displace sulphur in hydrogen sulphide, but between chlorine and oxygen theory indicates that an equilibrium might be produced. Gaseous chlorine ought to decompose water, when hydrated hydrochloric acid is formed, but, on the contrary,

oxygen ought to decompose anhydrous hydrochloric acid, with formation of water and chlorine.

1. A gaseous mixture of hydrogen chloride and oxygen, in proportion of 4 vols. of HCl and 1 vol. of O, was enclosed in a tube, and submitted to the action of the electric spark for some hours; nine-tenths of the mixture was decomposed, with formation of free chlorine and water.

2. Inversely, a weighed quantity of water, enclosed with free chlorine, was decomposed in a similar arrangement to the extent of one-tenth of the oxygen being liberated.

The former reaction takes place easily, when the mixed gases are passed through a red-hot porcelain tube, and the latter reaction, as is well known, occurs by itself at the ordinary temperature, especially in presence of solar light.

The theory was further verified by the author's experiments on the action of oxygen on hydrogen bromide and iodide; in both these cases, it should displace the halogen in the compound, whether the combination be gaseous or in solution; the results showed that the decomposition of the acid was complete at a temperature of 500°, whilst all attempts to effect the inverse action entirely failed.

In continuation of this subject (*ibid.*, **87**, 671—673), Berthelot draws attention again to facts which he has established, namely, that reciprocal displacements between acids united to one and the same base, are regulated entirely by the thermic value of the reaction, whenever the acid forms but one salt only, not decomposible by water, either wholly or in part; but that on the contrary there is a division of the base between the acids whenever the acid which evolves the greatest amount of heat forms with the base an acid or neutral salt, partially or progressively decomposible by the solvent. He now shows that this distribution also results when any two *weak* acids, such as hydrocyanic, boric, phenic, hydrosulphuric, or carbonic acid, react with an alkaline base.

Thus with hydrocyanic and boric acids we have—

KCN reacting with HBO_2 evolves 4·2 units.
KBO_2 „ „ HCN absorbs 2·9 „

the distribution of base being shown in the one case by a disengagement of heat; in the other by an absorption, the latter resulting from the partial decomposition of the reacting salts under the influence of the solvent.

In a similar manner, when potassium cyanide reacted with phenol, a division of base between the two acids took place, very nearly in the proportion of 2 : 5; with potassium phenate and boric acid, however, the latter almost entirely displaced the phenol.

Hydrosulphuric acid in presence of an excess of bicarbonate saturates itself almost completely, but with equivalent quantities it takes nearly seven-eighths of the base.

The total thermic effect in reactions of this kind is the resultant of two phenomena: (1) a disengagement of heat due to the combination of the acid with the free base; and (2) an absorption of heat due to the decomposition produced by the solvent. This resultant is generally, but not always, of contrary value for the two inverse actions. J. W.

Reaction between Mercury and Hydrochloric Acid Gas. By Berthelot (*Compt. rend.*, **87**, 673).—13·5 grams of mercury and 48 c.c. of pure and dry hydrogen chloride were sealed in a tube, and heated to as high a temperature as was possible for one hour. On opening the tube it was found that rather more than 1 c.c. of hydrogen had been formed, or about $\frac{1}{20}$th of the hydrochloric acid gas had been decomposed. J. W.

Inorganic Chemistry.

Formation of Ammonium Nitrite. By A. V. Lösecke (*Arch. Pharm.* [3], **14**, 54—58).—The author has corroborated Schönbeim's statement that the evaporation of water in air produces ammonium nitrite, and gives the results of experiments to determine the conditions of its formation. It is found that ammonium nitrite is always formed when water evaporates freely, and the lower the temperature the larger is the quantity produced; but the formation is prevented if the evaporation takes place in a narrow-necked flask. In another series of experiments, it was observed that 1 litre of water, evaporated to a small bulk, yielded ammonia equivalent to 0·148 part in 100,000 parts of water; 1 litre, evaporated to small bulk at 40—50°, yielded ammonia equivalent to 0·5823 part of nitric acid per 100,000 of water; and lastly, 5 litres of water, allowed to evaporate spontaneously, yielded ammonia equivalent to 2·9608 nitric acid per 100,000 parts of water. This last experiment shows the influence that the evaporation of rain-water and dew can have on the nourishment of plants; and it has been found that if a leaf be moistened and allowed to dry, nitrous acid is produced, and that in dew from leaves, ammonium nitrite can be easily detected. These experiments, therefore, explain the introduction of nitrogen into plants, which Boussingault says cannot occur directly. Ammonium nitrite can also be detected in snow and rain alone without contact with leaves, but then only in very minute quantities. The water used in the experiments was ascertained to be free from ammonia and also from nitric and nitrous acids. E. W. P.

Alkaline Reaction of Magnesium Carbonate and Silicate, Free, Mixed, and Combined. By Pichard (*Compt. rend.*, **87**, 797).—The natural and artificial carbonates of magnesia, whether free, mixed, or combined, give an alkaline reaction with litmus, the presence of $\frac{1}{1000}$th part in the mixture being sufficient to show it.

A few thousandth parts of natural silicate of magnesia are sufficient to give an alkaline reaction with litmus, whilst the silicates of potassium, sodium, and calcium are perfectly neutral. L. T. O'S.

On Chromates and Dichromates. By L. Schulerud (*J. pr. Chem.* [3], **19**, 36—41).—The results of the investigation show that only monad metals are capable of forming dichromates, and that as

lithium forms a dichromate, we have here an additional proof of the monatomicity of this element. Potassium chromate and dichromate produced identical precipitates in solutions of barium salts, although the wet precipitate from the dichromate was rather darker in colour; but the dichromate described in *Handwb. der Chemie*, **11**, 1235, as formed when barium chromate is dissolved in a chromic acid solution, could not be obtained; the calcium salt behaves similarly. Hot water withdraws chromic acid from the red silver dichromate. From neutral thallium carbonate, potassium dichromate precipitates a mixture of the chromate with the dichromate, whereas in acid solutions the dichromate only is formed. Lithium chromate, produced by the addition of lithium carbonate to chromic acid, crystallises in yellow prisms with 2 mols. of water; this is driven off at a temperature of 130°. The dichromate, which crystallises with 2 mols. of water, forms hard, almost black, thick plates; the crystalline water is driven off at 130°, and at a higher temperature the crystals melt and give off oxygen.

E. W. P.

The Oxide of Nickel, Ni_3O_4. By H. Baubigny (*Compt. rend.*, **87**, 1082—1084).—When oxygen is passed over nickel chloride at a temperature of 440°, the chloride is, after some time, completely transformed into a crystalline insoluble substance, which is no other than the oxide Ni_3O_4. The action is much more rapid with moist than with dry oxygen. This oxide of nickel, which is analogous to magnetic oxide of iron, cannot be made to furnish an oxide of a higher degree of oxidation, but by a strong heat it is reduced to the protoxide, NiO.

R. R.

Action of Haloïd Acids on Mercuric Sulphate, and of Sulphuric Acid on the Haloïd Salts of Mercury. By A. Ditte (*Compt. rend.*, **87**, 794—795).—By slowly heating mercuric sulphate in an atmosphere of hydrochloric acid gas, the gas is rapidly absorbed, and a compound is produced which melts and volatilises without decomposition, forming long white needles. On analysis, it was found to consist of equivalent quantities of mercuric sulphate and hydrochloric acid, $HgSO_4 + 2HCl$. The same compound is formed when mercuric sulphate is evaporated to dryness with strong hydrochloric acid. Unlike mercuric sulphate, this compound does not form a basic sulphate when treated with water, but is readily dissolved by it. This fact, together with the volatility of the substance, leads one to suppose that it consists of mercuric chloride united with a molecule of sulphuric acid, $HgCl_2 + H_2SO_4$, which is further confirmed by the fact that it may easily be prepared by treating mercuric chloride with sulphuric acid and warming the mixture, when the mass solidifies, and, on heating more strongly, volatilises, forming white needles.

Under similar conditions, a bromo-compound may be obtained from mercuric sulphate and hydrobromic acid, or mercuric bromide and sulphuric acid. It melts at a higher temperature than the chlorine compound, forming a yellow liquid, and finally sublimes in brilliant transparent plates. The action of hydriodic acid on mercuric sulphate, and of mercuric iodide on sulphuric acid does not yield a compound similar to the above (Souville, *Jour. Pharm.*, **26**, 474).

L. T. O'S.

Mineralogical Chemistry.

Microscopical Properties of Amber, and the Amount of Sulphur contained in it. By O. Helm (*Arch. Pharm.* [3], **13**, 496—503).—The clear yellow amber has no peculiar appearance when examined under the microscope; but if the opaque or white amber, cut into thin sections, be examined by a power of 200—500 diameters, round cavities, varying in size, are observed in the interior. The cavities in the milk-white amber are the smallest; in the opaque yellow sort they are larger; whilst in the less dense quality, the cavities present the appearance of a mass of soap bubbles. Water appears to be contained in the cavities, for if amber which has been laid in water for some time be exposed to an increased temperature, the weight of the specimen diminishes, from which it would appear that moisture can diffuse through the substance of the amber, and the insects which are enclosed in the substance are perfectly dry, owing to this diffusion. This peculiarity is turned to account by the amber merchants, who, to clean the amber, soak the pieces in boiling oil, whereby the cavities contract, and press out their contents, as water, lime, iron, &c. This process renders amber specifically heavier, transparent, and filled with innumerable small scale-like fissures.

Besides containing sulphur in the form of pyrites, amber likewise contains sulphur combined organically, and to the amount of 0·26 per cent. in the clear yellow sort, 0·38 in the dark, 0·34 in the bone-coloured, and 0·27 in the brownish-red weathered coating of the last-named kind. This sulphur is contained for the most part in the bitumen which is insoluble in alcohol or ether.

The author considers that the sulphur was introduced into the amber during the tertiary period, the origin being one of two, either the reduction of sulphates originally present in the interior, or that the sulphur has diffused itself into the resin from outside. In the first case the sulphate would be reduced to a sulphide, which in its turn would be transformed into an organic sulphide, and accompanied by the production of a metallic carbonate. The evidence of the original appearance and structure of the amber still existing unaltered renders the above internal chemical change improbable. It is therefore more likely that sulphuretted hydrogen, or some other easily decomposible sulphide, has been formed in the neighbourhood of the amber, and that this passing by diffusion into the interior then combines with the amber. E. W. P.

Gedanite, a New Fossil Resin. By O. Helm (*Arch. Pharm.* [3], **13**, 503—507).—Up to the present time, the substance known as "unripe amber" has been considered to be amber, but the author shows that it differs totally from true amber in its composition, and he has given it the name of gedanite. Gedanite has a hardness of 1½—2, breaks easily, and has a sp. gr. of 1·058—1·068. It does not contain succinic acid, and when heated in oil, it swells up and becomes like caoutchouc. Ether dissolves 40—52 per cent., and alcohol 18—25

per cent.; and of the residue left by evaporation of the alcohol, ether dissolves 20—24 per cent. The portion soluble in alcohol softens at 100°, and melts at 105°, and then resembles mastic. The ash amounts to 0·06 per cent, and consists of lime, silica, sulphuric acid, and ferric oxide. Sulphur organically combined appears also to be present, and, like amber, gedanite is negatively electric. Its composition is C 81·01, H 11·41, O 7·33, S 0·25. Gedanite therefore differs from amber in having a lower melting point, a smaller amount of oxygen, in being less hard, and more easily soluble in ether, and in the absence of succinic acid; and it differs from copal and other resins in containing sulphur organically combined, in having a higher melting point, and being less soluble in various liquids, and in its amber-like odour when heated. E. W. P.

On Asphalt and other Retinalites. By O. Hesse (*Arch. Pharm.* [3], **13**, 507—514).—To determine the amount of sulphur in asphalt-bitumen, and in what form the sulphur existed, whether as sulphates, or pyrites, or organic sulphur-compounds, a portion of asphalt was incinerated, and the sulphuric acid and iron were determined in the ash. Another portion treated with strong nitric acid gave the amount present as sulphide; and by the fusion of a third portion with sodium carbonate the amount of organic sulphur was determined. The experiments show that sulphates and sulphides are present only in very small quantity, whereas organic sulphur exists to the amount of 10·85 per cent. Sulphur is not found free in asphalt. It is probable that the formation of organic sulphur-compounds is due to the generation of sulphuretted hydrogen by the action of water and organic matter on calcium sulphate in the neighbourhood of the asphalt, which passes by diffusion into the interior of the mass, and then replaces oxygen by an equivalent of sulphur. The large amount of sulphur that was found organically combined in asphalt made it probable that experiments on coal would show that sulphur was also present there in a like state. Such proved to be the case, for when powdered coal was submitted to a temperature of 180°, a small amount of sulphuretted hydrogen was evolved, a slight rise of temperature produced a clear distillate, and at 320° an oil passed over, which turned brown in the air, and contained sulphur.

Elaterite contains 1 per cent. of organic sulphur, a yellow retinite 0·4 per cent., and iron only in traces. This specimen yielded free sulphuric acid when treated with water, the acid being formed by the oxidation of the sulphur compound on the surface. A specimen of walkowite gave strong indications of sulphuric acid when washed with water, and contained 0·72 per cent. of sulphuric acid, and 0·73 per cent. of organic sulphur. Under the microscope, a number of fine bubbles were seen in the interior of this specimen. Dopplerite and ozokerite contain no organically combined sulphur. E. W. P.

Organic Chemistry.

Action of Platinum Wire on Hydrocarbons. By J. Coquillon (*Compt. rend.*, **87**, 795—796).—The author has previously described the action of palladium wire on gaseous hydrocarbons in presence of aqueous vapour at a white heat, whereby carbonic oxide and hydrogen are formed. He finds that platinum wire under similar circumstances acts in like manner in presence of air with greater violence, explosions taking place when the quantity of hydrocarbon present exceeds 4 per cent., whereas with palladium, explosions do not take place unless 7 or 8 per cent. of hydrocarbon be present.

From experiments he finds that a mixture of marsh-gas and air is less explosive than a mixture of olefiant gas and air.

The author proposes to use platinum instead of palladium wires in his portable "grisoumètre" where the quantities of marsh-gas are small. L. T. O'S.

Action of Bromine on the Lower Paraffins. By V. Merz and W. Weith (*Deut. Chem. Ges. Ber.*, **11**, 2235—2243).—*Methane.*—Carbon tetrabromide is formed by slowly adding bromine to well-cooled methyl iodide, heating the mixture in sealed tubes at 80° and then gradually raising the temperature to 180°. The same compound is formed at the ordinary temperature by the action of bromine on carbon bisulphide in presence of iodine. It is, however, best prepared by the action of bromine on bromoform (Habermann, *Annalen*, **167**, 174).

Carbon tetrabromide splits up on distillation, forming tetrabromethylene, C_2Br_4, and bromine. Heated in sealed tubes at 350° it is decomposed into hexabromobenzene, C_6Br_6, and bromine.

Ethane.—The action of bromine on ethyl iodide, or on ethylene dibromide in presence of iodine at 250°, produces a mixture of tetrabromethylene (m. p. 52·5—53°), and hexbromethane, the former of which can be distilled in a current of steam. Hexbromethane begins to decompose at 180° into tetrabromethylene and bromine.

Propane.—Pentabromopropylene, prepared by heating a mixture of allyl bromide, bromine, and iodine at 210°, is an oily liquid which slowly distills in a current of steam. It decomposes at 180°, and is converted by the action of bromine at 250° into carbon di-, tri-, and tetra-bromides, C_2Br_4, C_2Br_6, CBr_4, and free bromine. W. C. W.

Action of Bromine on the Higher Paraffins. By V. Merz and W. Weith (*Deut. Chem. Ges. Ber.*, **11**, 2244—2253).—*Normal Butane.*—Bromine does not act on normal butyl iodide at 100°; at 140° a feeble action commences, which increases with the temperature, tetrabromethylene being formed, $C_4H_9Br + 8Br_2 = 2C_2Br_4 + 9HBr$.

Isobutane.—In presence of iodine, bromine attacks isobutyl bromide at the ordinary temperature, forming hexbromisobutane; the reaction takes place more rapidly at 150°. *Hexbromisobutane* crystallises in prisms or plates (m. p. 108°) which are soluble in carbon

bisulphide, in ether, and in hot alcohol. This compound is decomposed by bromine at 320—340°, forming hexbromo-butylene, $C_4H_2Br_6$ (m. p. 52—53°).

Isopentane.—On treatment with bromine at 175° isoamylene dibromide yields hexbromobenzene and a large quantity of a resinous product.

Hexane.—By the action of bromine on secondary hexyl iodide, at a temperature not exceeding 130°, a mixture of octobromhexane, $C_6H_6Br_8$ (m. p. 135°, according to Henry 140°), hexbromhexane, $C_6H_8Br_6$, and octobromhexylene, $C_6H_4Br_8$. Hexbromhexane crystallises in opaque prisms or needles (m. p. 152°), soluble in ether and in benzene. Octobromhexylene forms rhombohedral crystals (m. p. 178—184°), soluble in benzene. Between 130—140° carbon octobromide, C_6H_8, is formed. This compound is soluble in benzene, toluene, chloroform, carbon bisulphide, and in hot acetic acid, and is deposited from its solution in boiling benzene in glistening needle-shaped crystals, which decompose at 200° into bromine and hexbromobenzene. W. C. W.

Action of Chlorine Monoxide on Ethylene. By E. Mulder and G. J. W. Bremer (*Deut. Chem. Ges. Ber.*, **11**, 1958—1961).—A mixture of ethylene chloride and monochlorethyl monochloracetate, $C_4H_6Cl_2O_2$, is formed, when chlorine monoxide and dry ethylene are brought together in a well-cooled vessel. The monochloracetate boils with decomposition between 180° and 210°. When boiled with water it yields monochloracetic acid and glycol chlorhydrin—

$$CH_2Cl.CO.O.CH_2.CH_2Cl + H_2O = CH_2Cl.COOH + CH_2Cl.CH_2(OH).$$

W. C. W.

Potassium Cobaltocyanide. By A. Descamps (*Compt. rend.*, **87**, 1039).—When a cold solution of potassium cyanide is poured into one of cobalt chloride, avoiding excess, a reddish-brown precipitate of cobaltous cyanide is obtained, and this, carefully maintained at 0° is washed with water and dissolved in a solution of potassium cyanide also at 0°. The liquid is diluted with alcohol, and the next day it deposits deep blue amethyst-coloured crystals. These are washed with alcohol, and preserved in that liquid, as they decompose very readily. When they are mixed with a large quantity of water they are instantaneously converted into potassium cobaltocyanide, and the liquid gives with lead acetate an orange-yellow precipitate of lead cobaltocyanide, which may be preserved. With cobalt chloride, the author obtained a deep green precipitate, although his liquids were quite free from nickel. This green substance is the cobaltocyanide of cobalt and potassium, and when dissolved in potassium cyanide, it reproduces the cobaltocyanide. R. R.

Action of Carbonic Anhydride on Certain Cyamides. By G. Meyer (*J. pr. Chem.* [2], **18**, 419—429).—Drechsel (*ibid.* [2], **16**, 188 and 201) showed that the action of carbonic anhydride on an alkaline solution containing much ammonia is to produce carbamates, thus:—$NaNH_2 + CO.O = NH_2.CO.ONa$. This reaction has been fur-

ther experimented on by the author, who finds that cyamides absorb carbonic anhydride, producing cyamido-carbonates: these salts, like the carbonates, are easily decomposed, forming free cyanamides and carbonates. On passing carbonic anhydride into a boiling alcoholic solution of sodium cyamide, a bulky white precipitate was produced; this, when washed with alcohol and dried, was a white amorphous powder, consisting of sodium cyamidocarbonate, CNNaN.COONa. It is soluble in water, but separable from its aqueous solution by the addition of alcohol. The free acid cannot be obtained from the sodium compound, as it immediately breaks up into carbonic anhydride and cyanamide. The acid is apparently bibasic, CNHN.COOH, but by no method was it possible to obtain a salt containing but one atom of a monad metal. It appears also that the salts are polymerides of the cyanates, being converted into the latter when heated, NaCN.N.COONa = 2CNONa. If carbonic anhydride be passed into ether in which sodium cyamide is suspended, a large quantity of cyanamide is produced. This is due probably to the following reactions:—

(1.) $NaCNHN + CO_2 = CNHNCOONa$.
(2.) $CNHNCOONa + NaCNHN = CNNaNCOONa + H_2CNN$.

The potassium cyamido-carbonate has also been prepared, and with silver nitrate yields carbonic anhydride and silver cyanide. With other metallic salts like results are produced, so that it appears that the cyamido-carbonates of the heavy metals cannot be prepared.

Crude melam was ignited with powdered calcium oxide, the mass was then treated with water, and carbonic anhydride passed into the solution of calcium cyamide thus obtained; after some time calcium cyamido-carbonate separated out in fine stellate groups of needles. This salt, which readily decomposes by heat, crystallises with 5 mols. H_2O, and has therefore the formula $COOCaCNN + 5H_2O$. Dried at 130° calcium cyamido-carbonate loses 4 mols. H_2O, and from the residue ether extracts cyanamide, and water dicyandiamide; on heating it to 170° melamine sublimes: $COOCaCNN + H_2O = CaCO_3 + H_2CNN$.

The strontium salt, $4COOSrCyN + 9H_2O$, and the barium salt, $COOBaCyN + 1\frac{1}{2}H_2O$, have been obtained, but not the magnesium cyamido-carbonate. E. W. P.

Action of Diazo-compounds on Ethyl Mercaptan. By R. Schmitt and O. Mittenzwey (*J. pr. Chem.* [2], **18**, 192—195).—As the action of diazo-compounds on ethyl alcohol is known to give rise to aldehyde, it was expected that the thio-alcohol, under similar circumstances, would yield thio-aldehyde or thio-paraldehyde; this, however, is not the case; for when diazo-salicylic acid is heated with mercaptan at 170° in a sealed tube, ethyl disulphide is produced, the two nitrogen atoms of the diazo-compound being eliminated, thus:—

$$C_6H_3N_2O.COOH + 2(C_2H_5.SH) = C_6H_4(OH).COOH + (C_2H_5)_2S_2 + N_2.$$

M. M. P. M.

Action of Trimethylamine on Carbon Bisulphide. By A. Bleunard (*Compt. rend.*, **87**, 1040—1042).—A violent reaction

takes place when trimethylamine and carbon bisulphide are brought into contact; but by passing a current of trimethylamine into a mixture of alcohol and the bisulphide, a compound may easily be obtained, in colourless crystals belonging to the orthorhombic system. The results of analyses show that the reaction may be thus represented: $N(CH_3)_3 + CS_2 = N(CH_3)_3CS_2$. The crystals are therefore sulphocarbamate of trimethylamine. The substance melts at 125°, and is soluble in chloroform and in dilute alcohol, but it is insoluble in absolute alcohol, in sulphide of carbon, in ether, and in benzene. It dissociates at ordinary temperatures, and this dissociation increases in rapidity with the rise of temperature. Although concentrated acids destroy it by uniting with the trimethylamine and setting the carbon bisulphide at liberty, it readily forms compounds with dilute acids; with hydrochloric acid, forming the compound $N(CH_3)_3$, CS_2, HCll, and the additional half as much more acid gives another compound, $2N(CH_3)_3$, CS_2, 3HCI. It combines also with sulphuric, phosphoric, and nitric acids, and its reactions in general resemble those of the ureas. Mercuric chloride, and many other salts, unite with it in equivalent proportions. R. R.

Separation of Ethylamines. By E. Duvillier and A. Buisine (*Compt. rend.*, **88**, 31—34).—As in the preparation of diethyloxamide, a determinate quantity of oxalic ether is added to an aqueous, concentrated, and titrated solution of ethylated bases, in such proportion as to leave a slight excess of the bases in the mixture, which is maintained at 0°. After 24 hours, the diethyloxamide formed is separated by pressure, and the very alkaline mother-liquor is distilled on the water-bath, so as to collect the alcohol and bases which have not taken part in the reaction. On cooling, some diethyloxamide is deposited, and this is separated as before.

The authors did not find any ethyl diethyloxamate in the mother-liquors of the diethyloxamide when crystallised from water; yet the mixture of ethylated bases on which they operated contained a considerable quantity of diethylamine. On concentration, however, they obtained a syrupy liquid, which, when boiled with water, for a long time, and allowed to cool, yielded an abundant deposit of crystals of acid oxalate of diethylamine. The mother-liquor, now much less syrupy, yielded a fresh crop of crystals, when treated as before; and so on, several times in succession. The reaction consists in the transformation of the ethyl diethyloxamate into diethyloxamic acid, which during the long boiling, fixes a molecule of water, and is converted into hydrogen-ethylamine oxalate. R. R.

Action of Chlorocarbonic Ether on Halogen Compounds of the Fatty Acid Series. By O. J. Kelly (*Deut. Chem. Ges. Ber.*, **11**, 2220—2228).—When a mixture of chlorocarbonic ether and dibromallyl alcohol is heated with sodium amalgam, ethyl carbonate, propylene, carbonic oxide, and carbonic anhydride are formed.

On treating a mixture of dichlorhydrin and chlorocarbonic ether with sodium amalgam, carbonic oxide, carbonic anhydride, hydrochloric acid and ethylene are evolved, and a chlorinated ether, $C_6H_{10}Cl_2O_3$, and a small

quantity of ethyl carbonate, are obtained. The chlorinated ether is a heavy oil, which boils without decomposition at 225—230°. It is soluble in alcohol and in ether, but insoluble in water. It does not combine with bromine or with hydrobromic acid. On saponification with potash, glycerin and potassium carbonate are formed.

When epichlorhydrin is subjected to the action of chlorocarbonic ether and sodium-amalgam, carbonic oxide and anhydride are given off, and ethyl carbonate and an ether having the composition $C_6H_{10}O_3$ are formed. This latter compound boils at 145—150°, and has the sp. gr. 0·9931 at 21·5°. It is isomeric with ethyl acetoacetate, and has the formula, $O\begin{<}\begin{matrix}H_2C \\ | \\ HC—CH_2.COOC_2H_5\end{matrix}$, since it yields allyl alcohol, and not acetone, on saponification. W. C. W.

Action of Chloral Hydrate on Ammonium Thiocyanate. By M. Nencki and F. Schaffer (*J. pr. Chem.* [2], **18**, 430—432).—Nencki, by the action of chloracetic acid on ammonium thiocyanate, prepared a substance, $C_3H_3NS_2O$, which he calls rhodanic acid, and as this yields colouring matters when submitted to oxidation (*Chem. Soc. J.*), the reaction of thiocyanates with organic chlorine compounds has been examined. When ammonium thiocyanate is heated with chloral hydrate, the liquid darkens, and becomes solid on cooling, the reaction taking place according to the equation $2CCl_3.CH(OH)_2 + 2CNS.NH_4 = C_5H_5Cl_6N_3S + CNSH + 4H_2O$. The brown mass thus obtained leaves, on treatment with water, an insoluble residue, which crystallises from hot alcohol in long white needles; in the alcoholic mother-liquor is found a brown, resinous matter, the amount of which increases as the time of heating the two original substances is longer. The crystalline substance which separates from alcohol is insoluble in water, and only soluble to a very slight extent in cold alcohol or ether. Aqueous solutions of mineral acids or of alkalis have no effect on it, but warm sulphuric acid, potash, and soda decompose it. It does not melt, but decomposes at 180°; metallic oxides and iodine do not remove sulphur. This substance may be considered as a molecular grouping of thiocyanic acid with 2 mols. of the at present unknown trichlorethylidenimide, thus $(CCl_3.CHNH)_2CNSH$. It is concluded that the compound is not an ordinary thiocyanate, because it does not give the well-known ferric chloride reaction. E. W. P.

Paeonia Moutan. By Jagi (*Arch. Pharm.* [3], **13**, 335).—Ether extracts from the roots of this plant a white crystalline mass, which melts at 45°, and sublimes at a higher temperature. It is insoluble in cold water, but soluble in alcohol and ether, and gives definite reactions with the ordinary reagents. Analysis shows it to have a mol. weight of 169, which, from a comparison with that of capric acid, 172, renders it probable that it is a fatty acid, nearly related to capric acid, but of different melting point. E. W. P.

Conversion of Undecylenic Acid into Undecylic Acid. By F. Krafft (*Deut. Chem. Ges. Ber.*, **11**, 2218—2220).—*Undecylic acid*, $C_{11}H_{22}O_2$, prepared by heating undecylenic acid with red phosphorus

and hydriodic acid (b. p. 127°) at 200—220°, is a colourless, transparent substance, melting at 28·5°, and boiling at 228°, under a pressure of 160 mm. It is insoluble in water, but dissolves readily in alcohol and in ether. Barium and silver undecylates are insoluble in water.

W. C. W.

Some Derivatives of Arachidic Acid. By G. Tassinari (*Gazzetta chimica italiana*, **8**, 305—308).—*Arachidic acid*, $C_{20}H_{40}O_2$, crystallises in minute silky needles (m. p. 77°); very soluble in hot alcohol, but only sparingly in the cold. The potassium salt, when treated with acetic chloride, yields *aceto-arachidic anhydride*, $C_{22}H_{42}O_3$, crystallising in scales (m. p. 60°). *Valero-arachidic anhydride*, $C_{25}H_{48}O_3$, melts at 68°. *Arachidic chloride*, $C_{20}H_{39}OCl$, obtained by the action of phosphorus trichloride on the potassium salt, crystallises in silky scales (m. p. 66—67°); it is very alterable, decomposing even in dry air. Although concentrated nitric acid oxidises arachidic acid with violence, *nitro-arachidic acid*, $C_{20}H_{39}(NO_2)O_2$, may be prepared by mixing dry arachidic acid with powdered potassium nitrate, and adding sulphuric acid, taking care to cool well. It is easily soluble in ether, sparingly in cold alcohol, and melts at 70°. *Amido-arachidic acid*, $C_{20}H_{39}(NH_2)O_2$, obtained by the reduction of the nitro-compound with stannous chloride melts at 59°, and does not form compounds with acids.

C. E. G.

Dimethylacrylic Acid. By W. v. Miller (*Deut. Chem. Ges. Ber.*, **11**, 2216—2217).—*Dimethylacrylic acid*, $(CH_3)_2C{=}CH.COOH$ (m. p. 69·5—70°), prepared by the oxidation of isobutyl-formic acid, is identical with the angelic acid, which the author has previously obtained by the action of potassium permanganate on the valeric acid from fermentation amyl alcohol (*Ber.*, **11**, 1526; and this Journal, 1879, 45).

W. C. W.

Pyromeconic Acid. By H. Ost (*J. pr. Chem.* [3], **19**, 34—36).—Pyromeconic acid, $C_5H_4O_3$, the isomeride of pyromucic acid, is formed from meconic acid by elimination of 2 molecules of carbonic anhydride. Besides the normal salts of the general formula $C_5H_3MO_3$, it forms acid compounds of the formula $C_5H_3MO_3.C_5H_4O_3$, which easily part with a molecule of pyromeconic acid; both series of salts crystallise well, and have an alkaline reaction.

Pyromeconic acid combines with hydrochloric and sulphuric acids, but the compounds, $C_5H_4O_3 + HCl$, $C_5H_4O_3 + H_2SO_4$, and $2C_5H_4O_3 + H_2SO_4$, are decomposed by water and by alcohol. Nitric acid, in acetic solution, converts it into *nitropyromeconic acid*, $C_5H_3(NO_2)O_3$, which, when acted on by tin and hydrochloric acid, yields the hydrochloride of the corresponding amide, $C_5H_3(NH_2)O_3.HCl + H_2O$, crystallising in large prisms. With nitrous acid in ethereal solution, a compound of the formula $C_5H_3(NO)O_3 + C_5H_4O_3$ is obtained in citron-yellow crystals; this takes up a molecule of hydrogen when treated with an aqueous solution of sulphurous acid, and forms the compound $C_5H_5(NO)O_3 + C_5H_4O_3$, which crystallises readily. On boiling it with chloroform, a molecule of pyromeconic acid is removed, leaving *hydronitrosopyromeconic acid*, $C_5H_5(NO)O_3$. This is a moderately strong monobasic acid, displacing carbonic acid easily; like pyromeconic

acid, it forms two series of salts, and unites readily with hydrochloric and hydriodic acids. Hydronitrosopyromeconic acid is very readily oxidised, separating metallic silver from silver nitrate solution in the cold. By the action of reducing agents it is converted into a difficultly soluble amido-compound.

Pyromeconic acid and its derivatives are very easily acted on by alkalis, the slightest excess added to any neutral salt occasioning immediate decomposition, with production of formic acid. Concentrated nitric acid attacks it violently, hydrocyanic acid being amongst the products. C. E. G.

Two Monobromopyromucic Acids. By R. Schiff and G. Tassinari (*Gazzetta chimica italiana*, **8**, 297—302).—In studying the action of alcoholic potash on the addition-product of bromine and ethyl pyromucate (this Journal, 1878, abstr. 721), the authors find that two isomeric monobromopyromucic acids are produced, which are easily separated by taking advantage of their difference of solubility in boiling water, the acid previously described (m. p. 155°) being the most soluble. The new acid, which may be purified by crystallisation from a large quantity of water, or from dilute alcohol, forms beautiful micaceous scales (m. p. 180°). The acid of melting point 155°, when boiled with water for a short time, precipitated with hydrochloric acid, again boiled with water, and precipitated, repeating the operation six or eight times, is gradually converted into the isomeric acid (m. p. 180°). C. E. G.

Compounds of Aluminium Chloride with Benzene and Toluene. By H. Gustavson (*Deut. Chem. Ges. Ber.*, **11**, 2151—2152).—The compounds $Al_2Cl_6.6C_6H_6$, and $Al_2Cl_6.6C_7H_8$, are prepared by passing dry hydrochloric acid gas into a mixture of Al_2Cl_6 and the hydrocarbon. They are dense, orange-coloured liquids, which are decomposed by water. The sp. gr. of $Al_2Cl_6.6C_6H_6$ is 1·14 at 0°, and 1·12 at 20°; of $Al_2Cl_6.6C_7H_8$, is 1·08 at 0°, and 1·06 at 22°; the former solidifies at −5° to a crystalline mass, which melts at + 3°; the latter remains liquid at −17°. Both are violently attacked by bromine, the products of the action being respectively C_6Br_6 and $C_7Br_5H_3$. The author is of opinion that the syntheses recently effected by Friedel are determined by the formation of similar compounds. C. F. C.

Constitution of Cumic Compounds and of Cymene. By E. Paternò (*Gazzetta chimica italiana*, **8**, 289—292).—From the researches of Fittica and others, it is generally believed that camphor cymene is a normal propyl derivative, whilst the cumic compounds are isopropyl derivatives. Kraut, however, has recently shown (*Annalen*, **195**, 222) that cumic alcohol when boiled with zinc shavings, yields a cymene having the same sp. gr, and boiling point as camphor cymene; also that the barium salts of the sulphonic acids derived from these two cymenes appear to be identical. The author points out, however, that this identity in physical characters is not sufficient to establish identity in chemical constitution, as several instances are known where compounds of different chemical constitution have the same boiling point and specific gravity. It is almost certain that the isopropyl

group exists in the cumic compounds, if we consider the identity of natural cumene with synthetic isopropylbenzene, on the one hand, and the difference between it and normal propylbenzene, on the other.

C. E. G.

Crystalline-products Obtained from Pennsylvanian Petroleum. By L. Prunier and R. David.—A green crystalline body, obtained by the redistillation of petroleum which had furnished oils, sp. gr. 0·715 and 0·8, was exhibited at Philadelphia in 1876. It appears to be a mixture of the fluorescent colouring-matter of American petroleum and hydrocarbons derived from acetylene and benzene, and situated higher in the series than those already known. The percentage of carbon varies from 88—96. L. T. O'S.

Action of Nitrosyl-silver on Organic Bodies. By W. Zorn (*Deut. Chem. Ges. Ber.*, **11**, 2217—2218).—Nitrosyl-silver produces with ammonium chloride and the hydrochlorides of aniline and methylamine, a precipitate of silver chloride, and on warming the supernatant liquid a copious evolution of gas takes place. On the addition of nitrosyl-silver to an aqueous solution of phenol mixed with sulphuric acid, a yellowish-red coloration is produced. A yellow oil is obtained by adding nitrosyl-silver to a solution of ethyl acetoacetate in caustic soda. W. C. W.

Chloronitranilines. By F. Beilstein and A. Kurbatow (*Deut. Chem. Ges. Ber.*, **11**, 1978—1980).—

Nitrodichloranilines, $C_6H_2Cl_2(NO_2).NH_2$, with the chlorine atoms in the para-position.

Symmetrical nitroparadichloraniline, $NH_2:Cl:NO_2:Cl_2 = [1:2:4:5]$, and *consecutive nitrodichloraniline*, $NH_2:Cl:Cl:NO_2 = [1:2:5:6]$, are formed by nitrating the acetyl compound of paradichloraniline. The acetyl derivatives are separated by means of benzene, in which the *symmetrical* compound (m. p. 145°) is easily soluble. Symmetrical nitroparadichloraniline forms yellow needles, which melt at 153°. If the NH_2-group in this body is replaced by chlorine, symmetrical nitrotrichlorobenzene, $NO_2 : Cl : Cl : Cl : = 1 : 2 : 4 : 5$ (m. p. 58°), is formed. Consecutive nitroparadichloraniline, probably identical with Körner's nitro-dichloraniline from β-dinitroparadichlorobenzene (*Jahresb.*, 1875, 352), crystallises in pale yellow needles (m. p. 67°), and forms an acetyl derivative which melts at 204°. Consecutive nitro-trichlorobenzene, $NO_2 : Cl : Cl : Cl : = 1 : 2 : 3 : 6$, is obtained by replacing the NH_2-group in this body by chlorine.

Nitrodichloranilines, with the chlorine atoms in the ortho-position. (1) *Nitro-orthodichloraniline*, $NH_2 : Cl : Cl : NO_2 = [1 : 3 : 4 : 6]$, is obtained by heating symmetrical nitrotrichlorobenzene (m. p. 58°) with alcoholic ammonia at 200°. By nitrating unsymmetrical orthodichloracetanilide, a mixture of the acetyl derivatives of symmetrical and consecutive nitrodichloraniline, $NH_2:NO_2:Cl:Cl = [1:2:3:4]$, is formed. An alcoholic solution first deposits the former, then the latter compound; the mother-liquor contains a small quantity of the acetyl derivative of dinitrodichloraniline. Symmetrical nitro-orthodichloraniline crystallises in yellow needles (m. p. 175°), and yields

an acetyl-derivative which melts at 123°. It is converted into unsymmetrical nitro-orthodichlorobenzene (m. p. 43°) by the action of ethyl nitrite, and if the NH_2-group is replaced by chlorine, symmetrical nitrotrichlorobenzene (m. p. 58°) is formed.

(2) *Consecutive Nitro-orthodichloraniline*, $NH_2 : NO_2 : Cl : Cl = [1 : 2 : 3 : 4]$, melts at 95°; the acetyl compound melts at 152°.

Dinitrodichloraniline, probably $NH_2 : NO_2 : Cl : Cl : NO_2 = [1 : 2 : 3 : 4 : 6]$, crystallises in large red needles (m. p. 127°); the acetyl derivative melts at 245°.

(3) *The nitro-orthodichloraniline*, $NH_2 : Cl : Cl : NO_2 = [1 : 2 : 3 : 6]$, formed from consecutive nitrotrichlorobenzene (m. p. 55°), crystallises in yellow needles (m. p. 162°).

Nitrodichloranilines with the chlorine in the meta-position. (1) *Paranitro-metadichloraniline*, $NH_2 : Cl : NO_2 : Cl = [1 : 3 : 4 : 5]$, and the corresponding ortho-compound, $NH_2 : NO_2 : Cl : Cl = [1 : 2 : 3 : 5]$, are produced by the nitration of the acetyl-derivative of symmetrical metadichloraniline; (1) crystallises in yellow needles (m. p. 170°); its acetyl-derivative melts at 222°, and (2) forms yellow needles, which melt at 79°. Its acetyl-compound melts at 138°. (3) *Ortho-nitrometadichloraniline*, $NH_2 : Cl : Cl : NO_2 = [1 : 2 : 4 : 6]$, (m. p. 100°) and (4) *paranitrometadichloraniline*, $NH_2 : Cl : Cl : NO_2$ $[1 : 2 : 4 : 6]$, (m. p. 188°), have been prepared by Witt (*Ber.*, **7**, 1604, and **8**, 143).

Nitrochlorophenylenediamine, $NH_2 : NO_2 : NH_2 : Cl = [1 : 2 : 3 : 5]$, and not nitrodichloraniline, is formed by the action of alcoholic-ammonia on nitrotrichlorobenzene, $Cl : NO_2 : Cl : Cl = [1 : 2 : 3 : 5]$, (m. p. 68°).

Nitrotrichloranilines.—*Nitrotrichloraniline*,

$$NH_2 : NO_2 : Cl : Cl : Cl = [1 : 2 : 3 : 4 : 6],$$

prepared by nitrating the acetyl-derivative of unsymmetrical trichloraniline, melts at 124°; its acetyl compound melts at 193°. The derivative of symmetrical trichloraniline could not be obtained.

W. C. W.

Methylated Derivatives of Aniline and Toluidine, and the Colours obtained therefrom. By P. Monnet, F. Reverdin, and E. Nölting (*Deut. Chem. Ges. Ber.*, **11**, 2278).—The differences in the yield of methyl violet, when obtained from pure dimethylaniline or from a product also containing methylated toluidines, induced the authors to prepare the mono- and dimethyl- derivatives of aniline and the three toluidines in a state of purity, and to study their behaviour when subjected to the action of oxidising agents.

Monomethylaniline (b. p. 192°), prepared by reduction of methylphenyl-nitrosamine.

Dimethylaniline (b. p. 192°) solidified completely below 0°.

Monomethylorthotoluidine (b. p. 207—208°), sp. gr. 0·973 at 0°, combines with acetic anhydride, giving an acetyl compound, melting at 55—56°, and boiling at 260°. This was obtained by heating 750 grams of pure orthotoluidine, 400 grams of methyl alcohol, and 700 grams of hydrochloric acid for one day at 200—220°, and subsequent

transformation into the corresponding nitrosamine, which, on reduction, gives the pure base.

Dimethylorthotoluidine (b. p. 182—184°); obtained by heating 750 grams of orthotoluidine, 670 grams of methyl alcohol, 700 grams of hydrochloric acid for two days at 200—220°, and fractional distillation of the base obtained.

Mono- and *dimethyl-metatoluidine*, obtained by treating metatoluidine with methyl iodide, elimination of the excess of metatoluidine by treating the ethereal solution with sulphuric acid, and separation of the secondary and tertiary base by means of acetic anhydride. Both bases boil at 206—208°.

Mono- and *dimethyl-paratoluidine*, both boiling at 206—208°, have been prepared by Thomson, the tertiary base, also by Hofmann. Dimethylparatoluidine may be boiled with amyl nitrite without forming a nitroso-compound. All these bases give colour reactions with chloride of lime, and with chromic, iodic, and fuming nitric acids, for an accurate description of which the original paper must be consulted.

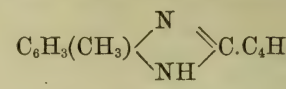
If these bases be treated with cupric chloride in the usual way, they all produce colouring matters, the quantity and quality of which were carefully estimated in each case. The derivative of dimethylaniline is the only one entirely soluble in water, and very considerable in quantity; whilst of the other bases only monomethylorthotoluidine gives a good yield. The colour of the derivatives of aniline and orthotoluidine is violet, whilst the para- and meta-toluidine derivatives give rise to brown colouring matters. O. N. W.

Action of Hydrogen on Metanitro-paratrichloraceto-toluide and Metanitro-paravaleryl-toluide. By T. Friederici (*Deut. Chem. Ges. Ber.*, **11**, 1970—1974).—*Metanitro-paratoluidine*, prepared by Kelbe's process (*Inaug. Dissert.*), crystallises from a dilute alcoholic solution in brick-red lustrous scales, and from a concentrated solution in needles or prisms, which melt at 114°. It forms crystalline salts with hydrochloric and nitric acids.

Metanitro-paratrichloraceto-toluide is prepared by gently warming in sealed tubes a mixture of metanitro-paratoluidine and trichloracetic chloride. The crude product is poured into a very dilute warm soda solution, and the yellow mass which is obtained is purified by crystallisation from hot alcohol. The pure substance crystallises in pale yellow glistening scales or prisms (m. p. 54°). By the reduction of nitrotrichloraceto-toluide with tin and hydrochloric acid, the author hoped to obtain a base having the composition, $C_6H_3(CH_3)\begin{cases} NH. \\ \\ N \end{cases}\!\!>\!C.CCl_3$, analogous to Hobrecker's anhydro-base, $C_6H_3(CH_3)\begin{cases} NH \\ \\ N \end{cases}\!\!>\!C.CH_3$, from metanitro-paraceto-toluide (*Ber.*, **5**, 920), but instead of this compound, acetic acid and toluylenediamine hydrochloride are formed.

$$C_6H_3.CH_3.NO_2.NH.CO.CCl_3 + 6H_2 = C_6H_3(CH_3)(NH_2.HCl)_2 + C_2H_4O_2 + H_2O + HCl.$$

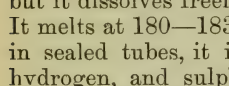
Metanitro-paravaleryl-toluide (m. p. 88°) yields on reduction with tin and hydrochloric acid, *anhydro-valeryldiamido-toluene*,



which crystallises in colourless prisms (m. p. 145°), soluble in alcohol, but insoluble in water. W. C. W.

Malachite Green. By O. Doebner (*Deut. Chem. Ges. Ber.*, **11**, 2274—2277).—The criticisms of E. and O. Fischer (*Ber.*, **11**, 2095) have led the author to repeat his experiments on the composition of malachite green (the product of the action of benzoyl trichloride on dimethylaniline). The results obtained confirm his previous conclusions, viz.: — (1) that malachite green has the composition $C_{23}H_{24}N_2$; (2) that the reduction-product, $C_{23}H_{26}N_2$, is identical with O. Fischer's tetramethyl-diamidotriphenylmethane (*Ber.*, **10**, 1624), prepared from dimethylaniline and benzaldehyde; (3) that the green colouring matter obtained by the oxidation of this base is not identical with malachite green. W. C. W.

Action of Sulphuric Anhydride on Phenylthiocarbimide. By G. Magatti (*Deut. Chem. Ges. Ber.*, **11**, 2267—2268).—When the vapour of sulphuric anhydride is passed over phenylthiocarbimide, sulphurous anhydride is evolved and a yellow crystalline precipitate, having the composition $C_7H_5NS_2O_3$, is formed. This substance is insoluble in water, alcohol, and ether, and also in acids and in alkalis; but it dissolves freely in hot benzene, nitrobenzene, and in chloroform. It melts at 180—183° with decomposition. Heated with water at 100° in sealed tubes, it is split up into carbonic anhydride, sulphuretted hydrogen, and sulphanilic acid. The author suggests that the constitution of this new compound may be represented by the formula



W. C. W.

Organic Thio-compounds. By O. Wallach (*Deut. Chem. Ges. Ber.*, **11**, 1590—1596).—Thiamides dissolve in alkalis, forming compounds which can be isolated to some extent in a crystalline condition. In this manner sodium thioacetanilide was obtained by dissolving thioacetanilide in sodium hydrate. The action of ethyl bromide on sodium thioacetanilide at 100° forms a peculiar-smelling oily product, which can also be obtained in a direct manner from thioacetanilide by mixing together alcoholic solutions of sodium and thioacetanilide (in the proportion of 1 mol. of the thiamide to 1 atom of sodium), then adding 1 mol. of ethyl bromide. Sodium bromide at once separates, and after distilling off the alcohol, the oily body is obtained by heating the residue in the vapour of steam. After drying over calcium chloride and redistillation, it boiled at 250° (uncorr.) and had the formula $C_{10}H_{13}SN$. When first obtained, it has a geranium-like odour, but it

soon acquires a disagreeable alliaceous smell. It is almost insoluble in water and in alkalis, but is miscible with alcohol and ether. From its solution in ether, gaseous hydrochloric acid precipitates a white mass, which is soluble in water, and gives a crystalline platinum salt of the formula $(C_{10}H_{13}NSHCl)_2PtCl_4$. It is decomposed by heating with dilute acids, yielding a pure aniline salt and a very volatile oil, which is specifically lighter than water, and insoluble in it; its alcoholic solution gives a white precipitate with mercuric chloride. Further investigation of this decomposition-product has to be made, but it probably contains the nucleus SC_2H_5.

The body which is formed by the action of ethyl bromide on sodium thioacetanilide may be represented either—(I) as $CH_3.CS.N(C_2H_5).C_6H_5$; or (II) as $CH_3.C(SC_2H_5)=NC_6H_5$. The author considers the second formula to be more probable, as from a body so constituted, aniline and thiacetic ether would easily be obtained, whilst the isomeric compound (1) would necessarily yield ethylaniline. This formula, moreover, represents a class of bodies which are isomeric with thiamides, and which should eventually be also obtained by the action of sodium mercaptide on acetanilide chloride. As thioacetanilide combines with ethyl bromide, forming a crystalline salt, which is decomposed by alkalis with production of a body apparently identical with the one above described, the author considers the following equation to represent the reaction in both cases:—$CH_3.CS.NH.C_6H_5 + C_2H_5Br = CH_3.CBr(SC_2H_5).NH.C_6H_5 = CH_3.C(SC_2H_5)=N.C_6H_5 + HBr$.

From these results it appears that the substituted thiamides can be very easily converted, by means of their sodium compounds, into thiocompounds of a new kind, which probably stand in the same relation to the thiamides as the thiocyanates to the oil of mustard.

The action of methyl iodide in a similar manner on an alkaline solution of thioacetanilide produces a colourless oil, having the formula $C_9H_{11}NS$; it boils at about 10° lower than its homologue, and behaves somewhat similarly. By the action of monochloracetic ether at a gentle heat on an alcoholic solution of sodium thioacetanilide, ethenyldiphenylamidine, $CH_3.C(NH.C_6H_5)=NC_6H_5$, is formed, together with an offensive smelling oil containing sulphur. A. J. C.

Preparation of Azobenzene from Aniline. By R. Schmitt (*J. pr. Chem.* [2], **18**, 195—198).—The author has already shown that paramidophenol hydrochloride is converted into dichlorazophenol by the action of bleaching powder. He now finds that aniline is converted into azobenzene by a similar reaction. Not more than 100 c.c. aniline should be employed in one experiment; 2 atoms of "available chlorine" are employed for each molecule of aniline. The aniline is diluted with 2 volumes of chloroform, and the mixture is added to the bleaching powder previously rubbed up also with 2 volumes of chloroform. The heat produced in the reaction causes the chloroform to distil off completely, after which the azobenzene may be obtained by distilling the residue. The reaction is not so sharp, however, as in the case of the paramidophenol, less than one-third of the aniline being converted into azobenzene. Toluidine yields azotoluene by a similar reaction. M. M. P. M.

Action of Fuming Nitric Acid and of Nitrous Acid on Benzene-sulphinic Acid. By W. Koenigs (*Deut. Chem. Ges. Ber.*, **11**, 1588—1590).—The author has not been able to obtain the two bodies of the formulæ $C_{18}H_{16}N_2S_3O_6$ and $C_{21}H_{22}N_2S_3O_6$ by the action of fuming nitric acid on benzene-sulphinic acid and toluene-sulphinic acid, as described by Otto and Ostrop (*Annalen*, **141**, 365), and by Otto and v. Gruber (*ibid.*, **145**, 19), but he finds that the action of fuming nitric acid or of nitrous acid on these sulphinic acids produces the body $C_{18}H_{15}NS_3O_7 = (C_6H_5SO_2)_3NO$, which he has previously obtained by the action of nitrous acid on dibenzsulphydroxamic acid,

$$(C_6H_5SO_2)_2HNO$$

(this Journal, 1878, Abs. 573).

The compound $(C_6H_5SO_2)_3NO$ has the same melting point and general properties as given by Otto and Ostrop for the body

$$C_{18}H_{16}N_2S_3O_6,$$

but contains only half the percentage of nitrogen required by the latter formula. It is difficultly soluble in alcohol and in dry ether, but dissolves easily at the ordinary temperature in chloroform and benzene. When heated with pure sulphuric acid, it yields a body which is soluble in water, and reduces Fehling's copper solution in the cold. Dibenzsulphydroxamic acid is converted into this body on being heated to about 90°, red fumes being evolved. A. J. C.

Derivatives of Orthonitrophenol. By J. Bendix (*Deut. Chem. Ges. Ber.*, **11**, 2262—2265).—*Oxyphenylthiocarbamide*,

$$C_6H_4(OH)HN(H_2N)CS,$$

prepared by warming a mixture of water, potassium thiocyanate, and orthoamidophenol hydrochloride, forms white crystals, which melt with decomposition at 161°. It is soluble in alcohol, ether, hot water, and in solutions of the alkalis. The hydrochloride forms a double salt with platinum chloride, having the composition

$$2[C_6H_4(OH)HN(H_2N)CS.HCl]2PtCl_4.$$

If too high a temperature is employed in preparing the thiocarbamide, decomposition takes place, ammonia and sulphuretted hydrogen are evolved, and needle-shaped crystals of *oxyphenylthiocarbimide* (m. p. 193°) are formed.

A *phenylene-carbamide*, having the composition $C_6H_4{=}(NH)_2{=}CO$, or $C_6H_4{=}N.CO.NH_2$, is formed by the action of mercuric oxide on an alkaline solution of oxyphenylthiocarbamide. This substance crystallises in white plates (m. p. 129—130°), which are soluble in water, alcohol, and ether. W. C. W.

Benzylated Cresol. By E. Paternò and G. Mazzara (*Gazzetta chimica italiana*, **8**, 303—305).—When some zinc turnings are added to a mixture of equal weights of paracresol and benzyl chloride, hydro-

chloric acid is evolved, and a liquid of a red-brown colour is obtained, from which *benzylated paracresol*, $C_6H_3(CH_3)(OH).CH_2.C_6H_5$, may be isolated by careful fractional distillation *in vacuo*. It is a transparent liquid, which distils unaltered at 240° under a pressure of 40 mm., but is decomposed when boiled under the ordinary pressure. It does not solidify at a low temperature, is only sparingly soluble in water, but readily in potash solution.

The *acetyl derivative*, $C_6H_3(CH_3)(OC_2H_3O).CH_2.C_6H_5$, prepared by the action of acetic chloride, is a colourless liquid, boiling at 245° under a pressure of 40 mm.

Benzylcresotic acid, $C_6H_5.CH_2.C_6H_2(CH_3)(OH).COOH$, is obtained by acting on the phenol with sodium and carbonic anhydride at 135—140°. It crystallises in needles (m. p. 164—166°), and gives a blue-violet coloration with ferric salts. C. E. G.

So-called Dichlorazophenol. By R. Hirsch (*Deut. Chem. Ges. Ber.*, **11**, 1980—1982).—The crystalline compound (m. p. 86°) which Schmitt and Bennewitz (*J. pr. Chem.*, **8**, 1) obtained by the action of bleaching powder on paramidophenol hydrochloride, yields salts of dichloramidophenol when dissolved in sulphuric or hydrochloric acid. By means of the diazo reaction, the sulphate was converted into dichlorophenol (m. p. 54°). These reactions lead the author to the conclusion that the compound of Schmitt and Bennewitz is not dichlorazophenol, $C_6H_3Cl(OH).N{=}N.(OH)ClC_6H_3$, but a chlorine substitution-product of a quinone imide, *e.g.*, $C_6H_3Cl(O)NH$.

W. C. W.

Action of some Diazosulphonic Acids on Phenols. By P. Griess (*Deut. Chem. Ges. Ber.*, **11**, 2191).—The author describes a number of sulphonated hydroxylated azo-compounds, some of which are well known colouring matters, and sold under different names, tropæoline, chrysoïdine, rocelline, &c. In enumerating these compounds we retain the nomenclature adopted by the author.

Parazosulphoxylbenzene - phenol, $C_6H_4(^{4}SO_3H)N^{1}{=}N^{1}.C_6H_4.^{4}OH$, obtained by acting on an alkaline solution of phenol with paradiazobenzenesulphonic acid. The free acid, which forms yellow prisms soluble in water and alcohol, is capable of forming two series of salts, normal and acid, most of which crystallise easily. The author describes the acid, potassium, and barium salts, and the neutral barium salt.

Metazosulphoxylbenzene - phenol, $C_6H_4(^{3}SO_3H)N^{1}{=}N^{1}.C_6H_4^{4}OH$.—This compound, isomeric with the previous one, is derived from the diazobenzenesulphonic acid, which may be obtained from Schmitt's metamidobenzenesulphonic acid.

Azobenzenesulphoxyl-phenol, $C_6H_5.N^{1}{=}N.C_6H_3.(^{3}SO_3H).^{4}OH$, is another isomeride, obtained by acting on orthophenolsulphonic acid with diazobenzene nitrate.

These isomerides split up, when subjected to the action of reducing agents, in the following manner: the first into paramidobenzenesulphonic acid and amidophenol; the second into metamidobenzene-

sulphonic acid and amidophenol; the third into aniline and amidophenolsulphonic acid.

Parazosulphoxylbenzene-orthonitrophenol,

$$C_6H_4(^{4}SO_3H)^{1}N{=}N.C_6H_3.{}^{2}NO_2{}^{4}OH.$$

This explosive compound is derived from paradiazobenzenesulphonic acid and orthonitrophenol.

Parazosulphoxylbenzene resorcin, $C_6H_4.(^{4}SO_3H).^{1}N{=}N.C_6H_3(OH)_2$, is formed by the action of paradiazobenzenesulphonic acid on a solution of resorcin in potash. On addition of acetic acid, the acid potassium salt crystallises out. A large excess of hydrochloric acid precipitates the free acid in the shape of small crystals, of steel colour. The acid sodium salt of this compound, which on reduction yields sulphanilic acid and amidoresorcin, is identical with Witt's tropæoline O (not R, as stated by mistake in the original paper).

Metazosulphoxylbenzene-resorcin, $C_6H_4(^{3}SO_3H)^{1}N{=}N.C_6H_3(OH)_2$, is the isomeride derived from Schmitt's diazobenzene sulphonic acid.

Parazosulphoxylbenzene-orcin, $C_6H_4(^{4}SO_3H)^{1}N{=}N.C_7H_5.(OH)_2$, similar to the resorcin compound.

Parazosulphoxylbenzene-salicylic acid,

$$C_6H_4(^{4}SO_3H)^{1}N{=}N^{4}C_6H_3(^{2}OH)(^{1}COOH).$$

Beautiful yellow needles.

Azosulphoxylxylene resorcin, $C_8H_8(SO_3H)N{=}N.(C_6H_3)(OH)_2$. Orange needles.

Metazosulphoxylbenzene α-naphthol and Metazosulphoxylbenzene β-naphthol, $C_6H_4(^{3}SO_3H)^{1}N{=}N.C_{10}H_6.OH$, both form small green crystals with metallic lustre, and are very similar in their appearance to

Azobenzeneβ-sulphoxyl-naphthol, $C_6H_5.N{=}N.C_{10}H_5(SO_3H)(OH)$, obtained by the action of diazobenzene nitrate on β-naphtholsulphonic acid. They are also isomeric with—

1. The compound obtained by acting with paradiazobenzenesulphonic acid on α-naphthol, sold under the names of tropæoline OOO No. 1, or orangé No. 1.

2. The corresponding derivative of β-naphthol, sold as orangé 2, or tropæoline OOO No. 2.

3. A compound prepared by A. W. Hofmann by acting with diazobenzene nitrate on α-naphtholsulphonic acid. There are altogether six isomerides known of the formula $C_{16}H_{12}N_2SO_4$, which may be distinguished by their different behaviour when subjected to reducing agents.

The author further prepared *parazosulphoxylbenzeneβ-naphtholsulphonic acid*, $C_6H_4(^{4}SO_3H)^{1}N{=}N.C_{10}H_5(SO_3H).(OH)$, by acting with paradiazobenzenesulphonic acid on β-naphtholsulphonic acid. The recrystallised barium salt, on decomposition with the theoretical quantity of sulphuric acid, yields the free acid, which is very soluble in water and alcohol.

Azonaphthalenesulphoxyl-β-naphthol, $C_{10}H_6(SO_3H)N{=}N.C_{10}H_6.OH$.

A pretty red colouring matter, obtained by the action of Clève's diazonaphthionic acid on β-naphthol.

A compound of *azosulphobenzoic acid* with *α-oxynaphthoic acid*,

$$C_6H_3(SO_3H).(COOH)N{=}N.C_{10}H_5(OH).(COOH),$$

obtained by acting with diazosulphobenzoic acid on Eller's α-oxynaphthoic acid, forms brown crystals slightly soluble in water.

Azodibromosulphoxylbenzene-dioxynaphthalene,

$$C_6H_2Br_2SO_3H.N{=}N.C_{10}H_5(OH)_2.$$

Violet crystals, soluble in water, with a yellow coloration.

O. N. W.

Azoxy-, Azo-, and Hydrazo-phenetols. By R. Schmitt and R. Mohlau (*J. pr. Chem.* [2], **18**, 198—204).—Paranitrophenetol in alcoholic solution is converted into parazophenetol when acted on by sodium amalgam. Orthonitrophenetol, however, yields a mixture of azophenetol and azoxyphenetol. The latter body crystallises in rhombic tables melting at 102°, and having the composition—

$$O\begin{<}\begin{matrix}N{-}C_6H_4.OC_2H_5\\ |\\ N{-}C_6H_4.OC_2H_5\end{matrix}.$$

Although the orthoazophenetol produced in this reaction is readily reduced to hydrazophenetol, $C_6H_4(OC_2H_5)NH.NH.C_6H_4(OC_2H_5)$, by the action of ammonium sulphide, parazophenetol does not undergo a similar change. Hydrochloric acid converts orthhydrazophenetol into a body which the authors believe to be orthodiamidodiphenetol, viz., $NH_2.C_6H_3(OC_2H_5).C_6H_3(OC_2H_5).NH_2$. M. M. P. M.

Pinacones and Pinacolins. Part IV. By W. Thörner and T. Zincke (*Deut. Chem. Ges. Ber.*, **11**, 1988—1993).—According to theory, acetophenone is capable of yielding three pinacolins, having the following formulæ:—

$$\text{(I.)}\ C_6H_5.(CH_3).C\begin{matrix}\diagdown\\ \\ \diagup\end{matrix}O;$$
$$C_6H_5.(CH_3)C$$

(II.) $(C_6H_5)(CH_3)_2C.CO.C_6H_5$; (III.) $(C_6H_5)_2(CH_3)C.CO.CH_3$;

but although several products are formed by the long-continued action of zinc and strong hydrochloric acid on an alcoholic solution of acetophenone, the authors have only succeeded in isolating one of the pinacolins, viz., III. The oily liquid boiling between 300° and 330°, which remains after distilling the crude product in a current of steam, to remove unaltered acetophenone, deposits crystals of acetophenonepinacoline. The mother-liquor yields, on fractional distillation, pinacoline, acetophenonepinacone, a substance melting at 107°, of unknown composition, and an oil boiling below 300°, which does not solidify, and may perhaps contain small quantities of the pinacolins I and II. *Pinacolin* III crystallises in rhombic prisms, which are soluble in benzene, chloroform, ether, and glacial acetic acid, and in hot alcohol. It melts at 41° and boils at 310°, and is decomposed by soda-lime into acetic acid and diphenylmethylmethane, $(C_6H_5)_2CH.CH_3$. This hydrocarbon boils at 264° and yields benzophenone on oxidation. It

is identical in its properties with the diphenylethane of Goldschmidt (*Ber.*, **6**, 1501), Radziszewsky (*ibid.*, **7**, 142), and Baeyer (*ibid.*, **7**, 1190). The pinacolin is reduced by the action of hydriodic acid and amorphous phosphorus, forming diphenylethylethane,

$$(C_6H_5)_2C(CH_3).C_2H_5.$$

This hydrocarbon crystallises in transparent plates or prisms (m. p. 127·5°), which are soluble in the usual solvents. It is identical in its properties with the hydrocarbon obtained from ethylbenzene bromide by Radziszewsky (*ibid.*, **7**, 140), and by Engler (*ibid.*, **7**, 1125). On oxidation the pinacolin yields diphenylmethylacetic acid, benzophenone, and benzoic acid. W. C. W.

Benzyl Orthothioformate. By M. Dennstedt (*Deut. Chem. Ges. Ber.*, **11**, 2265—2266).—*Benzyl orthothioformate*, $CH(C_7H_7S)_3$, prepared by the action of chloroform on an aqueous solution of sodium benzyl mercaptide, is a white crystalline body (m. p. 98°), soluble in ether, chloroform, and in hot alcohol. By the action of fuming hydrochloric acid at 250°, it is decomposed into formic acid and benzyl mercaptan. W. C. W.

Benzophenone. By W. Städel (*Liebig's Annalen*, **194**, 307—318).—Benzophenone, when heated with zinc-dust, is converted chiefly into diphenylmethane (m. p. 26°, b. p. 263°), thus confirming Græbe's results (*Ber.*, **8**, 1624), but it also yields in addition small quantities of tetraphenylethylene and tetraphenylethane. Barbier (*Compt. rend.*, **79**, 810), however, found that under apparently similar conditions benzophenone did not give diphenylmethane, but a liquid hydrocarbon (b. p. 270°), which did not solidify even in a freezing mixture, and which on heating to 500° gave no anthracene, but only toluene and a viscous liquid.

Tetraphenylethane, $C_{26}H_{22}$, crystallises in slender needles (m. p. 207°), which are sparingly soluble in alcohol. It is identical with the hydrocarbon obtained by Behr (*Ber.*, **3**, 751; **5**, 277) by the action of finely divided silver on benzophenone chloride.

Tetraphenylethylene, $C_{26}H_{20}$, crystallises in tables (m. p. 221°), and is identical with the hydrocarbon obtained by Græbe (*Ber.*, **8**, 1055) from benzopinacone and hydriodic acid, and by Zagoumenny (*ibid.*, **9**, 227), by the action of zinc and hydrochloric acid on benzhydrol, and by Thörner and Zincke (*ibid.*, **11**, 67), by treating benzopinacoline with phosphorus and hydriodic acid, and finally by Engler (*ibid.*, **11**, 926), from benzhydrol chloride.

Both of the above hydrocarbons give benzophenone on oxidation.

Benzophenonedisulphonic acid is obtained by the action of fuming sulphuric acid on benzophenone at a gentle heat. It is purified by means of the barium salt, $C_{13}H_8O(SO_3)_2Ba$, which is anhydrous, and crystallises in needles. The *potassium* and *sodium salts* cannot be easily crystallised on account of their great solubility in water. The copper salt crystallises in green plates.

The potassium salt when fused with potash gives paraoxybenzoic acid and phenol, together with a small quantity of an acid (probably dioxybenzoic), which is somewhat more soluble than paraoxybenzoic acid.

By the action of sulphuric on benzophenone there is likewise produced a second disulphonic acid, isomeric with the above. Its barium salt is more soluble than that of the latter compound, and separates in warty microscopic crystals. T. C.

Nitration of Benzophenone, Benzhydrol, and Diphenylmethane. By H. Praetorius (*Liebig's Annalen*, **194**, 338—372).—By acting on benzophenone with fuming nitric acid, sp. gr. 1·5, at a temperature of 60°, a product is obtained which may be separated into *α-dinitrobenzophenone* (m. p. 190°) and *β-dinitrobenzophenone* (m. p. 149°), by crystallisation from glacial acetic acid. The former of these crystallises in needles, and is less soluble in acetic acid than the β-compound crystallising in plates, which is obtained in by far the larger quantity. The product previously obtained by Chancel *Compt. rend.*, **28**, 83) by the nitration of benzophenone was therefore a mixture of the α- and β-compounds. The same two isomeric dinitrocompounds are also obtained by nitrating benzhydrol, and the α-compound also by the oxidation of Doer's dinitrodiphenylmethane (m. p. 183°). The β-compound (m. p. 149°) on reduction with tin and hydrochloric acid gives *β-diamidobenzophenone* (m. p. 165°), which is identical with the flavin obtained by Chancel and Laurent (*Annalen*, **72**, 280) on reducing their crude dinitrobenzophenone with ammonium sulphide. The β-diamido-compound when treated with acetic anhydride gives *diacetyldiamidobenzophenone*, $C_{17}H_{16}O_3N_2$, which crystallises in small colourless needles (m. p. 226°).

In addition to Doer's dinitrodiphenylmethane (m. p. 183°), the author has obtained an isomeric dinitro-compound by nitrating diphenylmethane. It is more soluble than the first compound, and crystallises in compact prisms (m. p. 118°).

The dinitrodiphenylmethane (m. p. 183°) on reduction with tin and hydrochloric acid gives *diamidodiphenylmethane* (m. p. 85°). The author is unable to confirm Doer's results, according to which an isodinitrodiphenylmethane (m. p. 172°) is obtained by the action of nitric acid, sp. gr. 1·4, on diphenylmethane. Doer's iso-compound is in fact a mixture of the two dinitrodiphenylmethanes, melting at 118° and 183° respectively, and benzophenone, the last being produced by the oxidation of the diphenylmethane.

On oxidation, dinitrodiphenylmethane (m. p. 118°) gives *γ-dinitrobenzophenone*, isomeric with the α- and β-compounds referred to above, and from which it is distinguished by its crystalline form, sparing solubility, and high melting point (196°). T. C.

Synthesis of Oxyketones by introducing Acid Radicles into Phenols. (Part II.) By O. Doerner and W. Stackmann (*Deut. Chem. Ges. Ber.*, **11**, 2268—2274).—Two *benzoresorcins* are obtained by the action of zinc chloride on a mixture of benzoic chloride and resorcin dibenzoate. The mixture is maintained at a temperature of 100—120° for several days, and the zinc chloride is added in small quantities at a time. After removing the excess of zinc chloride by boiling water, the crude product is saponified with alcoholic potash. The residue which remains on evaporating the alcohol is dissolved in water, and

carbonic anhydride passed through the aqueous solution. The portion of the oxyketone which is first precipitated is generally mixed with resinous matter, from which it can be separated by treatment with carbon bisulphide.

The benzoresorcin and dibenzoresorcin can easily be separated by recrystallisation from cold alcohol, in which the latter is but sparingly soluble.

Benzoresorcin, $C_6H_5.CO.C_6H_3(OH)_2$, crystallises in long needles (m. p. 144°), which are soluble in ether, alcohol, acetic acid, and also in hot water and in hot benzene. By the action of benzoic chloride a *dibenzoate*, $C_6H_5CO.C_6H_3(OC_7H_5O)_2$, is formed, which crystallises in colourless prisms, melting at 141°.

Dibenzoresorcin, $(C_6H_5.CO)_2C_6H_2(OH)_2$, crystallises in large colourless plates (m. p. 149°), which dissolve freely in ether, carbon bisulphide, benzene, and in hot alcohol. The *dibenzoate*,

$$(C_6H_5.CO)_2C_6H_2(OC_7H_5O)_2,$$

forms silky needles, which melt at 151°. The *diacetate*,

$$(C_6H_5.CO)_2C_6H_2(OC_2H_3O)_2,$$

crystallises in long glistening needles (m. p. 150°) which are soluble in ether, chloroform, carbon bisulphide, and in hot alcohol.

Stadel and Gail (*Ber.*, **10**, 746) have prepared a dioxybenzophenone which is an isomeride of benzoresorcin, moreover phenolphthaleïn is isomeric with dibenzoresorcin. W. C. W.

A Japanese Cinnamon-bark. By G. Martin (*Arch. Pharm.* [3], **13**, 337).—An essential oil can be obtained from this Japanese cinnamon-bark by distillation with steam. It is of a pale-yellow colour, lighter than water, and resembling ordinary oil of cinnamon in odour.

Concentrated sulphuric acid produces in it first a violet-red tint, which passes through indigo-blue, to a rich green, and finally becomes brown. If water is added to the blue liquid, the colour changes to green, and finally a green resinous substance separates, which is soluble in ether. Nitrobenzoic acid is not formed by the action of nitric acid on this oil, but solid soda changes the odour to that of camphor, and potassium permanganate produces an odour of oil of bitter almonds: the oil has a dextrorotatory power of 4°. E. W. P.

Oxidation of Aromatic Compounds. By A. Etard (*Compt. rend.*, **87**, 989—991).—The author has studied the action of chlorochromic acid on different aromatic bodies.

Bromotoluene.—By adding chlorochromic acid to excess of warm bromotoluene consisting of a mixture of para-, meta-, and ortho-compounds, hydrochloric acid is evolved, and the mass becomes pasty. After removing the chromium salts by washing with water, drying the oily product, and distilling, an oil was obtained which solidified on cooling. This was found to be parabromobenzoic acid (m. p. 250°). In this case the para-compound only was oxidised, the methyl group being destroyed, whilst the bromine remained unattacked.

Anethol.—Anethol, when treated in a similar manner to the above compound, yielded anisic aldehyde, $COH.C_6H_4.OCH_3$. The

allyl-group in the anethol, $C_3H_5.C_6H_4.OCH_3$, undergoing oxidation, whilst the methoxyl-group, OCH_3, remained unaltered.

Cymene.—Methylpropyl-benzene gives with chlorochromic acid a chocolate-brown precipitate, $2CrO_2Cl_2.C_{10}H_{14}$, which on dry distillation or decomposition with water yields a chlorinated compound. It is therefore probable that the chlorine is united to the carbon. When decomposed with water and allowed to stand for some time, a product is obtained which yields a hydrate of isocuminic aldehyde, $C_{10}H_{12}O + H_2O$, when distilled in a current of steam. It is a white crystalline body melting at 80°; above this temperature it loses its molecule of water and remains liquid. L. T. O'S.

Propylbenzoic Acid. By E. Paternò (*Deut. Chem. Ges. Ber.*, **11**, 2233).—The propylbenzoic acid, $C_6H_4(CH_2.CH_2.CH_3).COOH$, described by Körner (*Ber.*, **11**, 1863), was previously discovered by the author (*ibid.*, **10**, 1746). W. C. W.

Action of Cyanogen on Amidobenzoic and Anthranilic Acids in Aqueous Solution. By P. Griess (*Deut. Chem. Ges. Ber.*, **11**, 1985—1988).—When cyanogen is passed into an aqueous solution of metamidobenzoic acid, a mixture is formed of amidobenzoic acid percyanide, $CN.NH.C_6H_4.COOH.CN$, and *cyanocarbimid-amidobenzoic acid*, $3CN.CNH.NH.C_6H_4.COOH + H_2O$. The precipitate is treated with dilute hydrochloric acid, the solution saturated with ammonia, and the cyanocarbimid-amidobenzoic acid precipitated by the addition of acetic acid. This acid is insoluble in water, but soluble in alcohol; it is decomposed by boiling with acids or with water.

Dicyano-amidobenzoyl separates out when cyanogen is passed into a cold concentrated aqueous solution of anthranilic acid, $C_7H_7NO_2 + 2HCN = C_9H_5N_3O + H_2O$. It crystallises in yellowish prisms, which are sparingly soluble in cold alcohol, in ether, and in hot water, but dissolve readily in hot alcohol. The constitution of this compound is represented thus :—$NC.C<^{NH}_{N.CO}>C_6H_4$. W. C. W.

Metanitrocinnamic Acid. By R. Schiff (*Gazzetta chimica italiana*, **8**, 294—297).—It is known that when cinnamic acid is treated with nitric acid, two nitro-derivatives are formed, viz., ortho- and para-nitrocinnamic acids, and that these are respectively converted into ortho- and para-nitrobenzoic acids by the action of oxidising agents; but the metanitrocinnamic acid has not been prepared. Ordinary nitrobenzaldehyde is a meta-compound, and when it is digested with acetic anhydride and sodium acetate, the aldehyde group —COH becomes converted into the cinnamic group —CH=CH.COOH; in this way a crystalline mass of sodium metanitrocinnamate and sodium acetate is obtained. The free acid, $C_6H_4(NO_2).CH=CH.COOH$, forms a white crystalline powder (m. p. 196—197°). When oxidised it yields metanitrobenzoic acid (m. p. 140°). The silver salt is a white precipitate, and the ethyl salt forms lustrous slender needles (m. p. 78—79°), easily soluble in alcohol. C. E. G.

Phenylamidacetic Acid. By O. Stöckenius (*Deut. Chem. Ges. Ber.*, **11**, 2002—2004).—*Phenylamidacetic acid*, $C_6H_5.CH(NH_2).COOH$, prepared by the action of aqueous ammonia on phenylbromacetic acid, crystallises in pearly scales, which are insoluble in the usual solvents, but dissolve in acids, and in solutions of the alkalis and alkaline carbonates. It sublimes with partial decomposition without melting.

Hydrochloric, nitric, sulphuric, oxalic, and phosphoric acids unite with it to form crystalline compounds which are decomposed by water.

Benzaldehyde and a resinous product are formed by the action of phosphorus pentachloride on phenylamidacetic acid. W. C. W.

Diphenylmethylacetic Acid. By W. Thörner and T. Zincke (*Deut. Chem. Ges. Ber.*, **11**, 1993—1995).—*Diphenylmethylacetic acid* is prepared by heating acetophenone-pinacoline with a mixture of potassium dichromate and dilute sulphuric acid. The residue which remains after the benzophenone, benzoic acid, and unaltered pinacoline, have been removed by distillation in a current of steam, is filtered, and the green resinous mass treated repeatedly with a solution of soda. The acid is precipitated from the alkaline solution by hydrochloric acid, dissolved in ammonia, and reprecipitated.

If the crude oil, boiling between 300° and 325°, is used instead of the pure pinacoline for preparing diphenylmethylacetic acid, the acid will contain parabenzoylbenzoic acid, which can with difficulty be removed. Pure diphenylmethylacetic acid, $(C_6H_5)_2(CH_3)C.COOH$, is deposited from a solution in pure alcohol in glistening cubes, which are soluble in benzene, toluene, chloroform, and ether, and in hot alcohol and hot glacial acetic acid. This substance melts at 173°, and is volatile at a higher temperature.

The barium salt, $Ba(C_{15}H_{13}O_3)_2 + 2H_2O$, and the calcium salt, $Ca(C_{15}H_{13}O_2)_2 + 1\frac{1}{2}H_2O$, are deposited from a hot aqueous solution in long needles, which are sparingly soluble in hot water. The salts of the alkalis are very soluble in water.

On oxidation, the acid yields benzophenone, benzoic and carbonic acids. W. C. W.

Oxyphenylacetic Acid. By P. Fritzsche (*J. pr. Chem.* [2], **19**, 33).—The author has undertaken the investigation of oxyphenylacetic acid, $C_6H_5O.CH_2.COOH$, which was discovered and described by Heintz (*Pogg. Ann.*, **109**, 489), and named by him phenoxacetic acid. Heated with alcohol, this acid forms an ethyl salt boiling at 251°, and from this, the amide can be obtained by the action of ammonia solution. The calcium salt when submitted to dry distillation yields a liquid of high boiling point. Cold concentrated nitric acid converts oxyphenylacetic acid into the dinitro-derivative, $C_6H_3(NO_2)_2O.CH_2.COOH$. The mononitro-derivative may be obtained by the action of sodium monochloracetate on sodium-nitrophenol (prepared from the volatile nitrophenol). It melts at 153°, and is easily volatile in the vapour of water. E. W. P.

New Method of Preparing Phenylglyoxylic Acid. By L.

Claisen and F. H. Morley (*Deut. Chem. Ges. Ber.*, **11**, 1596—1598).—This acid can be obtained from the ethylphenylglyoxylate which is readily formed, together with mercuric monophenyl chloride, by the action of ethyloxalyl chloride on mercuric diphenyl in a sealed tube at 150—160°. The ethyloxalyl chloride used in the reaction was obtained by the action of phosphorus pentachloride on oxalic ether as described by v. Richter (*Ber.*, **10**, 2228).

By a similar reaction, naphthylglyoxylic acid can no doubt be obtained from mercuric dinaphthyl. A. J. C.

α-Oxyparatoluic Acid. By E. v. Gerichten and W. Rössler (*Deut. Chem. Ges. Ber.*, **11**, 1586—1588).—The authors have further examined the oxyparatoluic acid which they obtained from nitrotoluic acid (this Journal, 1878, Abs., 672), and proved to be identical with Flesch's oxyparatoluic acid prepared from sulphotoluic acid.

It crystallises in brilliant silky needles which are insoluble in chloroform, difficultly soluble in cold water, but easily in hot water, alcohol, or ether. It melts at 206—207° (corr.), and volatilises in the vapour of water: it gives no coloration with ferric chloride. The acid forms a characteristic lead salt which crystallises in small brilliant needles containing two molecules of water. *Barium* and *calcium salts* (the latter containing 4 mols. of water) have been obtained. The *ethyl salt* forms crystalline nodules which melt at 74—75°, and solidify at 60—62°. The *dimethyl salt* crystallising in needles and *methyloxytoluic acid* (m. p. 156°), have also been obtained. The latter crystallises in needles, and can be sublimed: it is insoluble in cold water but easily soluble in alcohol and in ether. The *barium salt* crystallises with 4 mols. water.

Orthocresol (b. p. 185—187°) was obtained by distilling the potassium salt with caustic lime: no decomposition occurred on heating the acid for some time with concentrated hydrochloric acid in a sealed tube, its behaviour in this respect being similar to that of metaoxybenzoic acid. Flesch's oxytoluic acid may be described as α-oxyparatoluic acid if under the term α-derivatives be included all the derivatives of paracymene and paratoluic acid in which the hydrogen in the nucleus of the substituting atom stands to methyl in the ortho position as $CH_3 : OH : COOH = [1 : 2 : 4]$, and this formula would represent the constitution of a series of compounds of paracymene and paratoluic acid in which it would be assumed that the admission of the negative atom (by the direct action of Cl, Br, &c.) or of complex atoms takes place in a similar manner. A. J. C.

Substituted Phthalanils. By S. Gabriel (*Deut. Chem. Ges. Ber.*, **11**, 2260—2262).—The following phthalanils were prepared by fusing phthalic anhydride with a substituted aniline: after the excess of phthalic anhydride has been removed from the crude product by boiling water, the residue is recrystallised from a suitable solvent.

Chlorophenylphthalimide (*para*), $C_6H_4Cl.N{=}(CO)_2{=}C_6H_4$, prepared from chloraniline (m. p. 64°) is deposited from a hot alcoholic solution in slender silky needles, which melt at 194°, and are soluble in benzene and in glacial acetic acid.

Bromophenylphthalimide (*para*), $C_6H_4Br.N{=}(CO)_2{=}C_6H_4$, from bromaniline (m. p. 65°) crystallises from an alcoholic solution in scales or needles, which melt at 203°. *Iodophenylphthalimide* (*para*), prepared from iodaniline (m. p. 60°) forms needle-shaped crystals (m. p. 227°) soluble in benzene and in glacial acetic acid.

Nitrophenylphthalimide (*meta*), $C_6H_4(NO)_2.N{=}(CO)_2{=}C_6H_4$, obtained from nitraniline (m. p. 110°) is deposited from boiling acetic acid in colourless needles (m. p. 242°). *Phthalimidobenzoic acid* (*ortho*), $HOOC.C_6H_4.N{=}(CO)_2{=}C_6H_4$, derived from anthranilic acid, crystallises in prisms (m. p. 217°) soluble in benzene, ether and glacial acetic acid. *Phthalimidobenzoic acid* (*meta*) prepared from amidobenzoic acid (m. p. 173°), melts at 276°, and is soluble in boiling alcohol and in acetic acid.

Diphthalimidodibromodiphenyl, $[C_6H_4(CO)_2N]_2(C_6H_3Br)_2$, formed by the action of phthalic anhydride on dibromobenzidine, melts at 300°, and is soluble in nitrobenzene and in glacial acetic acid. *Diphthalimidodiphenyl*, a yellow insoluble substance having a high melting point, is produced by the action of benzidine on phthalic anhydride.

W. C. W.

New Method of Preparing Chrysanisic Acid. By T. Friederici (*Deut. Chem. Ges. Ber.*, **11**, 1975—1977).—Chrysanisic acid is formed by the oxidation of dinitro-acetotoluîde, or better dinitrotoluidine (from metanitro-paratrichloracetotoluide) by potassium dichromate and dilute sulphuric acid. This mode of preparation confirms Salkowski's statement (*Ber.*, **10**, 1254) that chrysanisic acid is a dinitro-amidobenzoic acid, $C_6H_2(COOH)(NO_2)(NH_2)(NO_2) = [1 : 3 : 4 : 5]$.

W. C. W.

Dioxydiphenylmethane. By C. Beck (*Liebig's Annalen*, **194**, 318—333).—*Dioxydiphenylmethane*, $CH_2(C_6H_4.OH)_2$, is obtained by adding diphenylmethane gradually to a mixture of common and fuming sulphuric acid, and warming on a water-bath; 1 part of the potassium salt of the disulphonic acid thus produced is then fused with 2 parts of potash, and the fused mass dissolved in water; on the addition of dilute sulphuric acid, a precipitate of minute pearly plates, mixed with a resinous body is obtained. The hot solution of this precipitate, after filtering, deposited a quantity of pearly plates, consisting of dioxydiphenylmethane. The brown resinous body remained behind on the filter.

Dioxydiphenylmethane, after frequent crystallisation from water, separates in minute yellowish-white needles, instead of plates (m. p. 158°). These needles when placed in contact with the plates are again converted into the latter. Dioxydiphenylmethane is easily soluble in alcohol, ether and chloroform, but insoluble in carbon bisulphide. It is non-volatile in steam. The aqueous solution gives a yellowish-brown turbidity with ferric chloride, which on standing changes to a purple-red colouration.

The *potassium* compound, which is obtained when an ethereal solution of dioxydiphenylmethane is treated with an alcoholic solution of potash, is a white crystalline precipitate, which decomposes in contact with the air. The *normal* and *acid sodium* compounds are prepared by mixing a titrated alcoholic soda-solution with the calculated

quantity of the ethereal solution of the phenol. Both compounds are crystalline powders, and are easily soluble in water with a green colour, but difficultly soluble in ether. The *barium salt*, $CH_2(C_6H_4O)_2Ba$, forms small compact crystals. The following ethers were obtained by heating the corresponding potassium compound with methyl or ethyl iodide.

Dimethoxydiphenylmethane, $(C_6H_4.OCH_3)_2CH_2$, crystallises in plates (m. p. 49°; b. p. 330—340°). It is insoluble in water, but easily soluble in alcohol and ether. It appears to be identical with the compound obtained by Meer (*Jahrb. f. reine Chem.*, 1874, 420) from anisol and methylal.

Diethoxydiphenylmethane, $(C_6H_4.OC_2H_5)_2CH_2$ (m. p. 39°), is easily soluble in alcohol and ether, but insoluble in water.

Diacetoxydiphenylmethane, $(C_6H_4.O.C_2H_3O)_2CH_2$, is obtained by the action of acetic chloride on dioxydiphenylmethane. It crystallises in colourless prisms (m. p. 70°).

Dibenzoxydiphenylmethane, $(C_6H_4.O.CO.C_6H_5)_2CH_2$, is obtained in a manner similar to the acetyl compound; it crystallises in silky needles (m. p. 156°), which are insoluble in water, somewhat difficultly soluble in alcohol, but easily in ether.

Dioxydiphenylmethane is completely decomposed by the action of bromine vapour at the ordinary temperature, or by the action of aqueous bromine on its ethereal solution.

Tetrabromodioxydiphenylmethane, $C_{13}H_8Br_4O_2$, is obtained by acting on the phenol with bromine-water. It forms reddish crystalline plates (m. p. 225°), which are soluble in alcohol and ether. It is thrown down from its alcoholic solution by water as a white precipitate.

Dioxydiphenylmethane appears to form an addition-product when bromine is added drop by drop to its ethereal solution. It has probably the composition,—

$$C_{13}H_9Br_5O_2 = (OH.C_6H_2Br_2.CH_2.C_6H_2Br_2.OH)HBr.$$

In contact with the air it evolves hydrobromic acid, and dissolves in alcohol with formation of ethyl bromide: on adding water to this latter solution, crystals are precipitated which consist of $C_{13}H_8Br_4O_2$ (m. p. 221°), and are insoluble in water but soluble in alcohol and ether.

Dioxydiphenylmethane is completely destroyed on oxidation. The ethyl ether, however, when oxidised with chromic anhydride in glacial acetic acid, gives diethoxybenzophenone, $C_{17}H_{18}O_3$, which crystallises from alcohol in plates (m. p. 131°), and sublimes when strongly heated.

Dioxydiphenylmethane when heated for a long time with excess of potash at 300° gives phenol and paraoxybenzoic acid, proving that the two hydroxyls are in different benzene rings, thus:

$$HO.C_6H_4.CH_2.C_6H_4.OH + KOH + O_2 = OH.C_6H_4.COOK + H.C_6H_4.OH + H_2O.$$

T. C.

Oxidation of Dioxydiphenylmethane. By F. Gail (*Liebig's Annalen*, **194**, 334—337).—*Dibenzoxybenzophenone*, $CO(C_6H_4.O.C_7H_5O)_2$, is obtained when dibenzoxydiphenylmethane is oxidised with chromic

anhydride in glacial acetic acid. It crystallises in pearly plates (m. p. 182°), which are insoluble in water, little soluble in cold, and hardly soluble in hot alcohol or ether, but more soluble in glacial acetic acid and hot benzene.

Dioxybenzophenone, $CO(C_6H_4.OH)_2$, is easily prepared from the above compound by warming it with alcoholic potash. It crystallises from water either in thin plates or slender needles (m. p. 210°). It is but little soluble in cold water, but easily in hot water and in alcohol and ether; from alcohol it separates in compact monoclinic crystals, tables or prisms.

Diacetoxybenzophenone, $CO(C_6H_4.O.C_2H_3O)_2$, results from the oxidation of diacetoxydiphenylmethane, and may also be obtained by warming dioxybenzophenone with acetic chloride. It crystallises in brilliant needles (m. p. 152°), and is more soluble than the benzoyl compound.

When dioxybenzophenone, dissolved in alcohol, and mixed with 2 molecules of alcoholic potash, is heated on a water-bath with excess of ethyl iodide, a substance is produced which on crystallisation from alcohol separates in brilliant plates (m. p. 131°), consisting of the diethoxybenzophenone already described by Beck, whilst from the mother-liquor, compact crystals (m. p. 147°) are obtained on evaporation. This latter substance, which proved to be *monethyl-dioxybenzophenone*, $(C_6H_4.OH).CO.(C_6H_4.OC_2H_5)$, is easily soluble in alkalis, thus differing from the diethyoxy compound, which is insoluble in alkalis.

T. C.

Triphenylmethane. By E. and O. Fischer (*Deut. Chem. Ges. Ber.*, **11**, 1598—1599).—In continuation of their researches on the rosaniline derivatives (this Journal, 1878, Abs., 791), the authors have obtained *triphenylmethane cyanide*, and from it the corresponding *triphenylacetic acid* by the action of mercuric cyanide on triphenylmethane chloride at 170—180°. The cyanide crystallises from glacial acetic acid in fine colourless prisms (m. p. 137°): it is very stable, can be distilled without decomposition, and is unaltered when heated with concentrated hydrochloric acid at 170°. It saponifies with difficulty, giving with alcoholic potash a small quantity of *triphenylacetic acid*, and a considerable quantity of a new nitrogenous body crystallising in small white needles. *Triphenylacetic acid* can be, however, more easily obtained by the action of concentrated hydrochloric acid at 200—210° on the cyanide dissolved in glacial acetic acid: but even at this high temperature the decomposition of the cyanide is incomplete. It crystallises from glacial acetic acid in beautiful colourless rhombohedral crystals, and from alcohol in small needles.

A. J. C.

Chrysarobin in "Goa Powder." By C. Liebermann and P. Seidler (*Deut. Chem. Ges. Ber.*, **11**, 1603—1610).—The chrysophanic acid obtained by Attfield (this Journal, 1875, 1269) is said to be merely an oxidation product of *chrysarobin*, which the authors find to be the chief constituent of "Goa powder."

Chrysarobin extracted from Goa powder by means of boiling benzene crystallises from glacial acetic acid in small yellow laminæ, and can be

repeatedly crystallised without decomposition, proving it to be a somewhat stable body: but it is readily oxidised to chrysophanic acid by passing air through its solution in dilute potash, and in this way, by precipitating the alkaline solution with an acid and crystallising from petroleum spirit, pure chrysophanic acid can be obtained in large quantities.

Chrysarobin dissolves in concentrated sulphuric acid with a yellow colour, and with strong potash gives a yellow solution with dark green fluorescence, but it is insoluble in dilute potash. Chrysophanic acid on the other hand, gives red solutions with concentrated sulphuric acid and with dilute potash. By fusion with potash, chrysarobin yields a brown and chrysophanic acid a blue mass.

The formula for *chrysarobin* is $C_{30}H_{26}O_7$. The formation of chrysophanic acid from chrysarobin is expressed by the equation $C_{30}H_{26}O_7 + 2O_2 = 2C_{15}H_{10}O_4 + 3H_2O$.

Chrysarobin is converted into methylanthracene by ignition with zinc-dust.

Acetylchrysarobin, $C_{30}H_{22}O_7(C_2H_3O)_4$, is obtained by boiling chrysarobin with acetic anhydride and sodium acetate. It crystallises in yellowish prisms (m. p. 228—230°), which dissolve with difficulty in alcohol, the solution having a fine blue fluorescence, but they are easily soluble in glacial acetic acid. It becomes gradually oxidised to chrysophanic acid by boiling with alcoholic potash, and into diacetyl chrysophanic acid by boiling it with a glacial acetic acid solution of chromic acid. Fuming nitric acid converts it into tetranitrochrysophanic acid.

It has now to be ascertained whether the therapeutic action of Goa powder is due to chrysarobin or to its oxidised product chrysophanic acid. A. J. C.

Derivatives of the Hydrocarbon, $C_{16}H_{12}$, from Phenylglycol. By A. Breuer and T. Zincke (*Deut. Chem. Ges. Ber.*, **11**, 1995—2002).—The authors have described in a previous communication (*Ber.*, **11**, 1403) the hydrocarbon $C_{16}H_{12}$, and the quinone derived from it by oxidation with chromic acid.

The *oxyquinone*, $C_{16}H_{10}O_3$, precipitated on addition of hydrochloric acid to a solution of the quinone in warm soda, crystallises from a hot alcoholic solution in golden needles (m. p. 144°), which dissolve easily in ether, benzene, chloroform, and in hot alcohol. The oxyquinone is reprecipitated from its solution in strong sulphuric acid on dilution with water. This substance unites with bases to form salts having the formula $C_{16}H_9R'O_3$: the salts of metals of the potassium and calcium groups are soluble in alcohol. The *acetyl* derivative, $C_{16}H_9(OC_2H_3O)O_2$, crystallises in small yellow six-sided plates (m. p. 110°), which are soluble in alcohol and ether. The *benzoyl* compound, $C_{16}H_9(OC_7H_5O)O_2$, forms yellow monoclinic crystals (m. p. 120°) soluble in alcohol, ether, and chloroform. Aqueous sulphurous acid converts the oxyquinone into oxyquinhydrone, which is deposited from its benzene solution in steel-blue needles (m. p. 154°); but stannous chloride reduces the oxyquinone to *oxyhydroquinone* (m. p. 72°). On oxidation with potassium permanganate, or with potassium

dichromate and sulphuric acid, the oxyquinone forms benzoic and phthalic acids, whilst the quinone and the hydrocarbon, $C_{16}H_{12}$, under similar treatment, yield only benzoic acid.

Action of Ammonia on the Quinone.—A ruby-red crystalline compound having the composition $C_{16}H_9(OH)(O)NH$, separates out on the addition of ammonia to an alcoholic solution of the quinone. On diluting the mother-liquor with water, a second crop of crystals is obtained. The substance melts at 174°, and is readily soluble in chloroform, benzene, and ether. By the action of strong hydrochloric acid at 150°, or of caustic soda, it splits up into ammonia and oxyquinone.

The diacetyl-derivative forms glistening golden needles (m. p. 200°) soluble in chloroform and in benzene. W. C. W.

Derivatives of Terebenthene. By J. DE MONTGOLFIER (*Compt. rend.*, **87**, 840—842).—Berthelot obtained terpilene as the sole product of the action of sodium on terebenthene dihydrochloride; the author has studied the action of sodium on the monohydrochlorides, solid and liquid, with the following results.

(1.) *Solid Terebenthene Hydrochloride.*—By the action of sodium on the fused mono-hydrochloride a solid body is obtained, which after distillation over sodium, has great resemblance to camphene, but is a mixture of two hydrocarbons, namely, inactive camphene, which is present in the larger quantity, and a hydride of camphene of the formula $C_{10}H_{18}$; which possesses an odour and appearance somewhat similar to camphene, but is more crystalline. It melts at 120°, and is not attacked by ordinary or fuming sulphuric acid, or by fuming nitric acid. A third body is also formed at the same time, but in very small quantity: it may be isolated by treating the residue which remains after distillation with sodium, with water to separate the sodium, and then with ether. The ethereal solution is treated with animal charcoal, filtered and evaporated, when a viscous hydrocarbon remains: after purification over sodium, it becomes nearly colourless. It is a hydride of colophene of the formula $C_{20}H_{34}$; it melts at 322°, has the sp. gr. 0·9574 at 19°; it is dextrorotatory $[\alpha]_D = +21{\cdot}81$. It has a slight colour, but does not show dichroism; its odour resembles that of colophene, but it is more viscous. It is soluble in ether, in benzene, and in 8 parts of absolute alcohol, but is insoluble in alcohol of 95°, and in acetic acid. Sulphuric and hydrochloric acids do not attack it, and fuming nitric acid only slightly even when warmed.

By distilling solid terebenthene hydrochloride with mercuric oxide, camphene is formed, together with a small quantity of a liquid which is not terebene.

(2.) *Liquid Terebenthene Hydrochloride.*—This compound contained a small quantity of the dihydrochloride.

The product obtained by the action of sodium on the liquid monohydrochloride boils between 155—180°. The portion boiling between 155 and 165° is a liquid having the composition $C_{10}H_{18}$, containing a small quantity of the crystalline hydride of camphene. It has an odour resembling that of lemons, and a sp. gr. = 0·852 at 19°. It boils at 163°, and dissolves in fuming sulphuric acid, forming a sul-

phonic acid, the barium salt of which is very soluble; with fuming nitric acid it yields a nitro-derivative.

The portion boiling at 173° and above consists of a hydrocarbon, $C_{10}H_{16}$, which forms a liquid hydrochloride, and does not appear to differ from camphilene and teribelene. The author is continuing the study of the last two bodies. L. T. O'S.

Iodo-camphor. By A. Haller (*Compt. rend.*, **87**, 695).—With the view of preparing a cyano-derivative of camphor, a mixture of *iodo*-camphor and sodium-borneol in benzene, prepared according to the directions of Baubigny, was treated with cyanogen iodide, dissolved in the same liquid. Crystals were obtained which had the composition of iodo-camphor, whilst the liquid contained sodium cyanide and iodide. The crystals belonged to the clinorhombic system, were white, and insoluble in water, but soluble in alcohol, ether, and benzene. Their melting-point was 43—44°, but their solidifying point was as low as 28—29°. Analysis assigned to them the formula $C_{10}H_{15}IO$.

J. W.

Cyano-derivatives of Camphor. By A. Haller (*Compt. rend.*, **87**, 843—844).—By passing cyanogen gas into a mixture of camphor and sodium camphor dissolved in hot toluene, until the solution, which thickens and darkens in colour, begins to assume a red colour, a body is obtained, which may be isolated by washing the solution with water, separating the lower layer, which consists of a solution of sodium cyanide, and treating the remaining liquid with a dilute solution of soda, until the washings no longer give a precipitate with acetic acid. The washings are then mixed, and acetic or hydrochloric acid added: a white precipitate is thus formed, which is dried and crystallised from ether, when white rectangular prisms of the formula $C_{10}H_{15}(CN)O$ are obtained, or camphor in which one atom of hydrogen is replaced by the group CN. It is soluble in alcohol, ether, chloroform, and glacial acetic acid; it melts between 127—128°, volatilising slightly at the same time, and boils at 250°, when it begins to decompose.

Cyano-bromo-camphor.—This body is obtained by adding bromine to a solution of cyano-camphor in carbon bisulphide, in the proportions indicated by the following equation:—$C_{10}H_{15}(CN)O + Br_2 = HBr + C_{10}H_{14}Br(CN)O$, and exposing the mixture to sunlight. When hydrobromic acid ceases to be given off, the carbon bisulphide is removed by distillation, and the residue crystallised from alcohol. It is more soluble in alcohol, ether, and carbon bisulphide than cyano-camphor.

L. T. O'S.

Organic Ultramarines. By Forcrand (*Compt. rend.*, **88**, 30—31).—By heating metallic chlorides with the silver ultramarine, prepared in the way described by Heuman (*Ber.*, **10**, 291; *Bull. Soc. Chim.*, **28**, 570), the author has obtained silver chloride and ultramarines of various metals. He has now obtained ultramarines of organic radicles, by heating at 180° for 60 hours in a closed vessel, alcoholic iodides, with silver ultramarine. Ethyl ultramarine, prepared in this way, is a grey powder, which is decomposed when heated alone, giving off ethyl sulphide. R. R.

Investigation of the Seeds of Camellia Japonica. By KATZUJAMA (*Arch. Pharm.* [3], **13**, 334).—The seeds, after being freed from their oil by pressure, are exhausted with alcohol, the alcoholic solution precipitated by lead acetate, and the yellow precipitate thus produced decomposed by sulphuretted hydrogen; on evaporation, a white and blue powder of bitter taste is obtained, which the author calls *camellin*. This substance is almost insoluble in water, and when boiled with sulphuric acid, reduces alkaline copper solutions; it appears by other reactions to resemble digitalin, and has the molecular formula $C_{53}H_{84}O_{19}$. Boiled with dilute sulphuric acid, it yields only a small amount of sugar, showing that it is decomposed only with great difficulty, or else that other substances are produced. The alcoholic filtrate, after separation of the precipitate produced by lead acetate, leaves, when evaporated, a residue of a yellow colour, and bitter taste, which contains sugar and tannin, and perhaps another glucoside. The Japanese consider the seeds to be a poison, and the oil was formerly used to oil the swords of Japanese warriors. E. W. P.

Constituents of Ligustrum Ibotu. By G. MARTIN (*Arch. Pharm.* [3], **13**, 338—339).—The seeds of this plant resemble coffee in appearance, and contain a bitter, syrupy substance, which, when treated with sulphuric acid, reduces copper solution. The aqueous extract of the seeds gives a precipitate with lead acetate; and this, when decomposed with hydrogen sulphide and exhausted with alcohol, yields a solution which, when evaporated, leaves a yellowish-white powder, apparently a glucoside; sulphuric acid causes it to assume a red colour, which disappears on the addition of water. As this substance cannot be identified with syringin, it has received the name *ibotin*. The seeds contain 20 per cent. of an oil resembling olive oil, and the ash amounts to 3·422 per cent. E. W. P.

Two Isomerides of Santonin. By S. CANNIZZARO and CARNELUTTI (*Gazzetta chimica italiana*, **8**, 318—320).—On boiling santonin with hydriodic acid (b. p. 127°) and amorphous phosphorus, until hydrocarbons cease to be formed, removing these by distillation in a current of steam, concentrating the residue, and neutralising with sodium carbonate, a mixture of two isomerides of santonin is precipitated. This is purified by crystallisation from water and from ether, and the crystals of the two isomerides separated mechanically. The long flexible needles are metasantonine (m. p. 160·5°), already described (*Gazzetta*, **4**, 452), whilst the large hard prisms (m. p. 136°*) are a new isomeride, $C_{15}H_{18}O_3$. Both these compounds are very stable, and have the same rotatory power; they are not sensibly acted on by acetic anhydride or chloride, or by phosphorus trichloride. They both yield monobrominated derivatives by the action of bromine; the *monobromometasantonin* crystallises in silky needles, melting at 212°, whilst the corresponding brominated isomeride melts at 114°.

C. E. G.

* In another part of the paper the melting-point is given as 130°.—C. E. G.

Santonin Derivatives. By S. Cannizzaro and L. Valente (*Gazzetta chimica italiana*, **8**, 309—318).—The addition of the elements of water to santonin, $C_{15}H_{18}O_3$, gives rise to a bibasic acid, *photosantonic acid* (Sestini, *Gazzetta*, **6**, 357), and to four isomeric monobasic acids, $C_{15}H_{20}O_4$, viz., the *santoninic acid* of Hesse (*Ber.*, **6**, 1280), the *santonic acid* of Cannizarro and Sestini (*Gazzetta*, **3**, 241), *metasantonic acid* (*ibid.*, **6**, 345), and *parasantonic acid*. These four monobasic acids differ not only in their crystalline form, solubility, and other physical characters, but also in their behaviour with reagents.

Santonic acid, when treated with phosphorous trichloride, gives rise to *santonic chloride*, $C_{15}H_{19}O_3Cl$ (m. p. 170—171°); the corresponding *iodide* fuses at 136°, and the *bromide* at 145·5°. By passing hydrochloric acid into a solution of santonic acid in methyl or ethyl alcohol, or by the action of the haloïd paraffins on metallic santonates, *methyl santonate* (m. p. 86—86·5), and *ethyl santonate* (m. p. 94—95°) are readily obtained. By the action of nascent hydrogen, sodium santonate is transformed into the sodium salt of *hydrosantonic acid*, $C_{15}H_{22}O_4$, the silver salt of which yields metasantonic acid (*Gazzetta*, **6**, 345). This isomeride of santonic acid, however, may be more conveniently prepared by distilling santonic acid under a diminished pressure of 52 to 43 mm., stopping the distillation as soon as the distillate becomes coloured, and the boiling point rises. Both the distillate and the residue in the retort are dissolved in a solution of sodium carbonate, and after agitation with ether to remove oily matters, the alkaline solution is precipitated with an acid, and the metasantonic acid purified by crystallisation from ether. Metasantonic acid is also formed by the action of alkaline solutions on santonide. *Metasantonic chloride*, $C_{15}H_{19}O_3Cl$, prepared by the action of acetic chloride or of phosphorus trichloride on metasantonic acid, crystallises in slender needles (m. p. 139°), moderately soluble in ether. *Methyl metasantonate* forms large, lustrous crystals (m. p. 101·5—102·5°). It is prepared by passing hydrochloric acid into a methyl alcohol solution of metasantonic acid.

Santonide.—If a solution of santonic acid in glacial acetic acid is boiled for several hours, and the acid is then distilled off until the temperature rises to 180°, a residue is left, which solidifies on cooling to a viscous mass of the colour of amber. This residue is agitated with ether and an aqueous solution of carbonate of soda, the ethereal solution decanted and evaporated, and the santonide thus obtained is purified by repeated crystallisation from ether. Santonide, $C_{15}H_{18}O_3$, melts at 127—127·5°. The quantity obtained forms but a small proportion of the product, the greater proportion consisting of unchanged santonic acid, which is dissolved by the alkaline solution.

Parasantonide.—This substance, isomeric with that just described, is prepared and purified in a similar manner, but the distillation is continued until the temperature rises to 260°. It melts at 110—110·5°. Both santonide and parasantonide are lævorotatory, but santonide acts the more energetically on the polarised ray.

Parasantonic Acid.—This acid is prepared from parasantonide by boiling it with soda solution, precipitating with an acid, and purifying by crystallisation from ether or from water. It may also be obtained by decomposing the parasantonide with boiling dilute hydrochloric

acid. The free acid forms large white crystals, which are moderately soluble in ether and in water. It is a powerful acid, easily expelling carbonic acid from its salts. The parasantonates are mostly very soluble in water and in alcohol, and difficult to obtain in the crystalline state. The *barium* salt, $(C_{15}H_{19}O_4)_2Ba$, forms slender needles. Parasantonic acid, when treated with acetic chloride or phosphorus trichloride, does not yield the corresponding chloride, but is converted into parasantonide. *Methyl parasantonate* crystallises in hard prisms (m. p. 183—184°). *Ethyl parasantonate* forms colourless needles (m. p. 172°), only sparingly soluble in ether.

Hydrosantonide, $C_{15}H_{20}O_3$.—This compound may be prepared from hydrosantonic acid and purified in a manner precisely similar to santonide and parasantonide, but is obtained in much larger quantity if the hydrosantonic acid be first heated with glacial acetic acid in closed tubes at about 150°, for four hours. It is a crystalline substance, melting at 155—156°. C. E. G.

Cinchotenicine. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 1983—1985).—When cinchotenine sulphate is heated at 140—150°, it is converted into the isomeric cinchotenicine sulphate. The free base obtained by the action of baryta-water on the sulphate, is a dark brown, brittle, amorphous mass, which is insoluble in ether, but dissolves in water, alcohol, chloroform, dilute acids, and in alkalis. The aqueous solution has a bitter taste, and is dextrogyratory and neutral to litmus paper. The hydrochloride gives yellow, amorphous precipitates with platinum chloride, gold chloride, and potassium picrate; with phosphotungstic acid it produces a flesh-coloured precipitate, insoluble in dilute hydrochloric acid. W. C. W.

Alstonia Bark. By O. Hesse (*Deut. Chem. Ges. Ber.*, **11**, 2234—2235).—The bark of *Alstonia constricta* contains from 2 to 2·5 per cent. of chlorogenine, and 0·1 per cent. of porphyrine. The author considers that Palm's alstonine (*Wittstein's Viertel Jahresbericht f. pr. Pharm.*, **12**, 161) is a mixture of these two alkaloïds, and that the alstonine recently described by Mueller and Rummel (this Journal, 1879, 31) is probably impure chlorogenine. W. C. W.

The Basic Constituent of Dita Bark (Alstonia or Echites scholaris). By E. Harnack (*Deut. Chem. Ges. Ber.*, **11**, 2004—2007).—In reply to the remarks of Hesse (*Ber.*, **11**, 1546) the author states that dita bark contains only one base, *ditaïne*, which is a basic glucoside, having the composition $C_{22}H_{30}N_2O_4$. The base is best obtained by precipitating the alcoholic extract of dita bark with phosphotungstic acid. *Ditaïne* is soluble in water, alcohol, and chloroform, and sparingly soluble in benzene and ether. The hydrochloride crystallises in long needles, soluble in hot water and in alcohol. This salt gives a red coloration with strong sulphuric acid, and with nitric acid a green coloration, which afterwards turns red. It is precipitated by lead acetate, in presence of ammonia.

A beautiful carmine-coloured base is formed by the action of concen-

trated nitric acid on ditaïne. The hydrochloride has a red colour, and is very unstable. W. C. W.

Scopolia Japonica. By G. Martin (*Arch. Pharm.* [3], **13**, 336).—This plant stands between Solanum and Atropa in the Solanaceous family, and its roots are employed by Japanese physicians for the same purpose as Europeans use *Atropa belladona;* but its effects are not so powerful as those of *A. belladona.* The roots contain no atropine, but solanine is present; moreover the plant is remarkable in being highly fluorescent. E. W. P.

Evodia Glauca. By G. Martin (*Arch. Pharm.* [3], **13**, 337).—The bark of *Evodia glauca* (*Rutaceæ*) is of a pale-yellow colour slightly tinged with green, and covered with a cork-like epidermis; it is easily broken, soft, can be readily separated into layers, has a very bitter taste, and contains berberine in large quantity. The evodia is employed largely in Japan as a drug and also as a dye-stuff.

E. W. P.

Cholic Acid. By A. Destrem (*Compt. rend.*, **87**, 880).—By distilling cholic acid, $C_{24}H_{40}O_8$, with zinc-dust, a hydrocarbon, $C_{24}H_{32}$, is obtained, which begins to distil at about 215°, the temperature gradually rising to 325°. The last portions are very viscous, and sometimes small crystals are deposited in the neck of the retort.

By the oxidation of cholic acid with potassium permanganate in the cold, there is formed, besides oxalic and butyric acid and other products, an acid having the composition $C_{24}H_{36}O_{15}$. This acid when dried in a vacuum forms a vitreous mass very soluble in water and alcohol, but only sparingly in ether. It forms an ethereal salt when its alcoholic solution is treated with hydrochloric acid gas.

L. T. O'S.

Hæmocyanin, from the Blood of the Octopus Vulgaris. By L. Fredericq (*Compt. rend.*, **87**, 996—998).—The liquid portion of the blood of the *Octopus vulgaris* contains an albuminoïd which unites with oxygen, forming a blue compound; it loses its oxygen when in contact with animal tissues, or if kept in a closed space or in a vacuum; it plays the same part in the respiration of the octopus that hæmoglobin does in the respiration of vertebrata, that of a carrier of oxygen. It is a colloïd, and being the only colloïd present in the blood, it may easily be isolated by subjecting the plasma to dialysis, filtering, and evaporating the solution at a low temperature, when hæmocyanine is obtained as a brilliant blue mass having the consistence of gelatin.

It is the only albuminoïd contained in the blood of the octopus, and may be coagulated by heat in presence of common salt at 69°, the liquid becoming opalescent at 68°, also by alcohol, ether, tannin, mineral acids, salts of the heavy metals, silver nitrate, copper sulphate, and basic and neutral lead acetate. It gives the characteristic reactions for the albuminoïds with Millon's reagent, nitric acid, and ammonia, and with potassium ferrocyanide and acetic acid. After ignition it leaves a residue containing copper, which appears to be present in the same state as iron in hæmoglobin, and to play the same part. As hæmoglobin can be decomposed into hæmatin and an albuminoïd con-

taining no iron, so likewise by the action of hydrochloric and nitric acids, may hæmocyanin be resolved into a coagulated albuminoïd and a liquid yielding prismatic crystals, which after ignition leave a residue of copper.

The author has not determined the quantity of copper present in the hæmocyanine. L. T. O'S.

Physiological Chemistry.

Modification Effected by the Animal Organism on various Albuminoïd Substances when Injected into the Veins. By J. Béchamp and E. Baltus (*Ann. Chim. Phys.* [5], **14**, 512—543).—Having shown that several varieties of albumin unquestionably exist, differing from each other, not only in rotatory power but also in their power of inducing fermentation, and in the manner in which they are affected by various reagents, the authors proceed to study the effect of the animal organism on these albumins, by injecting solutions into the veins, and subsequently examining the liquid excreta.

The isolation and purification of the various albumins with which the experiments were conducted are carefully described in detail. Three albumins were obtained from white of egg, and termed triplumbic albumin, hexplumbic albumin, and zymase, respectively; two also from blood serum, hexplumbic albumin, and a zymase. Another variety or modification was obtained by the purification of ordinary gelatin. The method adopted for separating albumin from the urine or other liquid after it had passed through the system, consisted in adding to one volume of urine three volumes of strong alcohol and a few decigrams of sodium acetate; having allowed the solution to remain at rest for 24 hours, the deposit was collected on a filter, washed with alcohol, and subsequently dissolved in water, acetic acid, or solution of sodium carbonate. The liquid was then in a suitable condition for examination with the polarimeter.

The proportion of ash and zymase naturally contained in the urine of healthy dogs was first determined; also the effect of injecting several hundred cubic centimeters of water into the femoral artery, in order to eliminate any causes of error which otherwise might have arisen under these heads.

In the first two experiments 18 grams of white of egg dissolved in several c.c. of water were injected; of this 10·255 grams were excreted unaltered, the rotatory power of the albumin before injection being −41·42°, and of the same after separation from the urine −41·5°.

In five cases in which albumin from blood serum was injected, either in the natural state or dissolved in water, no albumin was eliminated in the urine. The injection of this substance produced serious derangement of the system, and in one instance death ensued. Pure triplumbic albumin of known rotatory power and free from ash, was injected into the right femoral artery of three dogs, and the urines

were examined as in the previous instances. The results observed were, that this albumin introduced into the circulation, either in dilute or concentrated solutions, was not eliminated, or at least only in very small quantity; and, further, that the trace of albumin excreted did not present the characters of that which was injected, since it was not coagulable, either by heat or by alcohol. The injection of pure hexplumbic albumin was tried in one instance. The results were precisely similar to those in which triplumbic albumin was used.

The substitution of hexplumbic albumin prepared from the serum of bullock's blood, did not modify the results. In three cases no albumin was found in the urine, whilst in one instance in which albumin was unquestionably found, it was at the same time shown that the animal was greatly affected by the injection, was suffering from urethritis, and that its urine was in a morbid condition.

The injection into the veins of solutions of ordinary gelatin, or of gelatin rendered soluble in cold water, was found to produce violent congestion of the alimentary canal and kidneys, and frequently to cause the death of the animal under experiment. In those cases in which death did not ensue, the quantity of urine excreted was greatly diminished, and no gelatin was eliminated.

The foregoing instances serve to show that in a study of this description, it is by no means a matter of indifference whether the experiments are conducted with a mixture of albumins or with isolated albumins; and, further, the manner in which the albuminoïd substances behave in the system depends upon their specific nature, and not upon the quantity injected. J. W.

Oxalic Acid not Poisonous (?) By E. Pfeiffer (*Arch. Pharm.* [3], **13**, 544).—Uppmann has stated (*Allgs. Med. Central. Ztg.*, 1877) that the notion that oxalic acid is poisonous is erroneous, since he found that doses of 1 gram of oxalic acid were insufficient to kill a dog. The author denies Uppmann's conclusions, for seeing that a large quantity of calcium phosphate is usually present in the stomach of a dog, it is most probable that the oxalic acid is converted into insoluble calcium oxalate by double decomposition, and recommends that the experiments be made on rabbits. E. W. P.

Danger of Employing Methyl Alcohol in certain Industries. By C. Poincaré (*Compt. rend.*, **87**, 682).—Some animals which had remained from 8 to 16 months in an atmosphere continually renewed, but charged with a certain quantity of methyl alcohol vapour, were afflicted with great increase in size of the abdomen, together with other serious symptoms. On examination after death, there was found to be considerable hypertrophy of the liver, which filled the greater part of the abdominal cavity; a fatty degeneration of this organ to an extent that could scarcely be exaggerated; an alteration of the constitution of the muscular fibres of the heart, of the epithelial cells, of the uriniferous tubes, and of a large number of the cells of the lungs.

The author does not state whether the methyl alcohol had been mixed with ethyl alcohol, or was in the condition of "wood spirit,"

but he argues against the introduction of methylated spirit into certain industries, as likely to prove very injurious to the workmen.

J. W.

Chemistry of Vegetable Physiology and Agriculture.

Inversion and Alcoholic Fermentation of Cane Sugar. By U. Gayon (*Compt. rend.*, **86**, 52—54).—Cane sugar is readily inverted by certain ferments, such as *Penicillium glaucum* and *Aspergillus niger;* several specimens of *Mucor*, however (*M. mucedo*, *M. circinelloïdes*, &c.), have no action on the sugar. In making experiments with the latter ferments, great care must be taken to obtain them perfectly pure.

Two species, *M. spinosus* and *M. circinelloïdes*, were especially studied; they have a similar action on beer wort, but the second is much the more active. When these bodies are placed in liquids without free oxygen, their mycelium takes the form of cells which multiply with great rapidity; the mycelium reverts to the ordinary form directly the liquid is aërated.

In solutions of glucose and lævulose, alcoholic fermentation is set up, as in beer wort, but in a solution of cane sugar there is no fermentation; if, however, spores of *Torulas*, or of any other ferment capable of inverting cane sugar be added, the ordinary alcoholic fermentation commences; it is therefore shown that cane sugar is not directly fermentable. F. D. B.

Region of the Solar Spectrum which is Indispensable to Vegetable Life. By P. Bert (*Compt. rend.*, **87**, 695—697).—Some growing plants placed under a green glass shade quickly languished and died, whereas similar plants under a red glass flourished, apparently without receiving much detriment.

On examining these coloured glasses with the spectroscope, it was found that the red glass intercepted the yellow and all the more refrangible portion of the spectrum, allowing only the orange and red rays to pass, whilst the green glass allowed every ray to pass, with the exception of about three-fourths of the red, starting from the left end of the spectrum.

By comparing the green glass with a solution of chlorophyll, it appeared that in the red portion of the spectrum which the glass obliterated there was included exactly the most characteristic absorption-band of chlorophyll; the assumption therefore seemed probable that this was the portion of the spectrum which, being absorbed by the leaf, was most indispensable to its life. By way of testing this hypothesis, some plants illuminated by a good diffused light were surrounded by hollow glass shades containing an alcoholic solution of chlorophyll, which was continually renewed. The plants immediately ceased to grow and gradually perished. The solution surrounding them, which was very weak and in a thin layer, intercepted effectively

only a narrow section of the red portion of the spectrum, allowing every other ray to pass.

Although this portion of the spectrum comprised between the rays B and C is necessary to vegetable life, it would be an exaggeration to say that it was sufficient for it. A plant will live for a long time under a red glass, but it does not thrive vigorously; the total deprivation of blue-violet rays causes it to throw out sickly shoots, and eventually to lose a good deal of its colour, so that there is no difficulty in recognising it as a plant which has not enjoyed the benefit of full daylight. It would prove a very protracted investigation, but not the less interesting, to attempt to prove that every region of the solar spectrum contains rays which play some active part in the life of a plant, and that the simultaneous action of the whole, exactly balanced in the proportion to form white light, is necessary to assure vital harmony, and thereby to conduce to a healthy vegetable life. J. W.

Ripening of Rye. By A. Müntz (*Compt. rend.*, **87**, 679—682).—The milky liquid contained in the grain of unripe rye was expressed, precipitated by basic lead acetate, filtered, and evaporated to the consistency of a syrup. The syrup was treated with concentrated alcohol, which precipitated a white amorphous mass; this latter was purified by dissolving it in water and repeating several times the precipitation by alcohol. The aqueous solution of this substance did not rotate the plane of a ray of polarised light nor reduce Fehling's liquor. Heated to 100° with a 2 per cent. sulphuric acid for two or three minutes it became strongly lævorotatory, −53°, and easily reduced the copper solution: by treatment with milk of lime, the sugar was isolated in the usual way and found to be ordinary lævulose.

The author terms the substance as existing in the rye, *synanthrose*, having isolated the same sugar-producing body from several plants belonging to the order *Synantherecæ*. The synanthrose gradually disappears as the plant ripens, being converted into starch. Thus, at a certain period, the grain contained 45 per cent. of synanthrose and 24·55 per cent. of starch; five months later, the same plant contained 5·19 per cent. of synanthrose and 70·45 per cent. of starch. The whole of the synanthrose does not, however, disappear, from 2 to 5 per cent. being always present, the larger portion of which is contained in the husk or bran. As the other cereals do not contain this peculiar body, it is very easy to recognise in the meal the fraudulent addition of rye flour. Rye contains neither inulin nor dextrin, but derives its starch solely from this substance. J. W.

Nitrates in Beetroots. By J. A. Barral (*Compt. rend.*, **87**, 1084—1087).—The author has analysed some enormous English beetroots which were sent to the Agricultural Society of France. The large quantity of nitrates and small quantity of sugar contained in these, as compared with French beetroots, are shown in the following results extracted from a table given in the paper:—

Name of Root.	Weight of the root.	Dry residue per cent.	Nitrates, estimated as KNO_3, per cent. in dry residue.	Sugar per cent. in dry residue.	Albuminoïd matters per cent. in dry residue.
	Kilos.				
Sutton's "Mammoth"	14·15	5·81	13·89	17·21	22·13
„ "Berkshire"	10·60	7·95	4·28	25·16	20·43
„ "Cœur-de-Bœuf"	11·39	6·35	9·21	31·50	21·51
„ "Tankard"	8·92	7·88	11·39	12·69	19·52
Dumoutier's "*Globe Jaune*"	2·08	11·54	1·37	34·66	9·43
„ "*Corne-de-Bœuf*" ..	1·78	12·60	0·64	31·75	8·07
„ "*Disette géante*" ..	2·44	9·46	0·68	52·86	10·91
„ "*Blanche à collet vert*"	3·12	11·92	0·13	58·72	6·91

The author calculates that the food of an animal kept on these large English beetroots would contain a quantity of nitre which might be positively injurious. The source of the large quantities of nitrates which these beetroots take from the soil, the author believes to be the abundant manure to which a very large proportion of nitrate of sodium has been added. In France the sugar manufacturers prohibit the growers of beetroot from using this salt. R. R.

Ash of the Garden Pink and Rose. By R. Andreasch (*J. pr. Chem.* [2], **18**, 204—207).

I. *Pink* (*Dianthus caryophyllus*).

	Roots.	Stalks.	Leaves.	Flowers.
K_2O	23·33	23·00	35·51	49·41
Na_2O.....	0·85	—	—	—
CaO	45·26	45·16	27·69	5·85
MgO.....	4·43	5·48	8·27	3·68
Fe_2O_3	3·83	7·95	6·42	7·19
Mn_3O_4	—	—	—	traces
Al_2O_3	2·56	traces	—	—
P_2O_5.....	11·22	10·25	10·94	14·84
SO_3	2·59	6·46	4·59	4·04
SiO_2.....	5·34	0·61	3·71	4·25
NaCl	0·59	0·44	0·71	2·35
KCl	—	0·65	2·16	8·39
	100·00	100·00	100·00	100·00
Percentage of ash ..	5·64	5·26	4·44	5·59

II. *Rose* (*Rosa remontana*).

	Roots.	Stalks.	Leaves.	Flowers.
K_2O	13·45	14·25	33·13	47·41
Na_2O.....	4·01	0·15	0·69	1·95
CaO	40·88	51·50	31·29	13·25
MgO.....	7·15	7·62	9·23	5·34
Fe_2O_3	2·86	4·23	2·49	0·97
Mn_3O_4	—	—	traces	traces
Al_2O_3	traces	—	—	—
P_2O_5	29·14	10·62	11·68	25·46
SO_3	1·95	2·22	4·31	3·17
SiO_2	0·21	4·85	5·71	1·52
NaCl.....	0·35	4·56	1·47	0·93
KCl	—	—	—	—
	100·00	100·00	100·00	100·00
Percentage of ash..	2·04	2·31	9·43	6·27

M. M. P. M.

Absorptive Power of Soils and of Silica. By J. M. v. Bemmelen (*Deut. Chem. Ges. Ber.*, **11**, 2228—2233).—In a previous communication (*Landw. Versuchs. Stat.*, **21**, 135—191; this Journal, 1878, Abs., 598—604), the author has shown that a soil which has been boiled with hydrochloric acid can absorb only a very small quantity of potassium from a solution of potassium chloride, although it can take up considerable quantities of potash or of potassium carbonate. If this soil be boiled with sodium carbonate and thoroughly washed with water, its power of absorbing potassium from a solution of potassium chloride will be restored. A quantity of sodium equivalent to the potassium absorbed passed into solution. The absorptive power of the soil is also restored, to a slight extent, by treatment with calcium sulphate or chloride.

From the results of a series of experiments, the author concludes that the absorptive power of the soil is due not to physical, but to purely chemical causes. The absorption of the base from a solution of a salt containing a powerful acid is due to double decomposition with the basic silicates in the soil; but the absorption of free alkalis and their compounds with feeble acids is owing to their combination with hydrated silicic acid to form insoluble silicates. W. C. W.

Influence of Soils on the Decomposition of Organic Substances. By J. Soyka (*Zeitschr. f. Biologie*, **14**, 449—482).—The influence of soils of varying character upon the nitrification of urine has been experimentally studied by the author. He finds that nitric acid may be detected, after 6 weeks, in urine which has been allowed to remain in contact with broken glass; after the same time, when ignited soil is used instead of glass; and after 8 days, when the same soil, but unignited, is employed. That the porosity of a soil largely influences its power of nitrification is shown by comparing the results

obtained with a given soil, with those obtained after the pores of the same soil have been filled with liquid. In one case the urine was poured on to soil contained in a glass tube, until the latter was filled with the mixture. In the other case the soil was drenched with urine, which was then poured off, and this process was repeated daily, the excess of urine being returned to the main quantity. The results were as follows:—

	Nitric acid appeared in	
	Porous soil.	Non-porous soil.
Urine 10 times diluted ..	After 7 days.	After 23 days.
„ 100 „ „ ..	„ 5 „	„ 27 „

Similar differences were noticed in the times required for the production of nitrous acid by the porous and by the non-porous soil.

Further experiments were conducted with gravels of varying degrees of fineness. These showed that the smaller the particles composing the soil, or, in other words, the greater the capillarity of the soil, the greater is the amount of nitrogen oxidised to nitrites and nitrates in a given time. Thus the following numbers were obtained:—

Diameter of soil grains.	Pores. Minimum water capacity*: In percentage of total volume of soil.		N as HNO_2 and HNO_3 per litre of urine. After 18 days.	After 36 days.
4—6 mm.	35·0	5·7	190 mgm.	480 mgm.
2—4 „	36·4	7·17	480 „	660 „
1·2—2 „	36·9	13·6	680 „	
0·6—1·2 „	37·9	29·8	860 „	1060 „

That a soil whose capillary pores are filled with urine causes a greater amount of nitrification in a given time than the same soil when completely drenched with urine, was also shown by an arrangement of tubes, in one of which the level of the urine was decreased from day to day, while the other was kept constantly filled with the liquid. No nitric acid could be detected in the second tube after 3 months, whilst in the first a considerable amount of nitrification had taken place. A considerable increase in the amount of nitric acid formed in a given time was noticed when the tubes were artificially ventilated. If, however, ignited soil and filtered air were employed, no nitrification occurred even after 3 months. When ignited soil was used and free access of air was allowed, nitric acid was detected after 28 days; with the same soil and access of filtered air, nitric acid was absent even after 3 months. When broken glass mixed with ordinary soil was employed, nitric acid appeared after 7 days, whilst if the soil was ignited before use, nitric acid did not appear until after 6 weeks. These results show that although nitrification may be brought about by the agency of the matter present in ordinary air, the main agent is nevertheless to be found in the soil itself.

When soil was added to urine which had been previously boiled,

* This expression is used by the author to denote the volume of liquid retained in the soil after thoroughly wetting it and pouring off the excess of liquid.

nitric acid was produced after some time. If, however, the mixture of soil and urine was boiled, no acid made its appearance, even after long intervals of time.

A larger quantity of nitric acid was produced when the experiments were conducted in darkness than in ordinary daylight. The more dilute the urine, the greater the amount of nitrification, other conditions being constant.

In one instance decrease of temperature was accompanied with an increase in the amount of nitric acid produced. This experiment was, however, conducted in a corridor with open doors leading to the outer air. The author thinks that the ozone probably present under these conditions caused a more rapid oxidation of the nitrogen of the urine.

As the amount of nitric acid in river water is evidently largely dependent upon the nature of the soil, the degree of äeration of the water, the time which has elapsed since sewage entered the river, &c., the author thinks that great care should be exercised in coming to conclusions concerning previous contamination of river waters from determinations of the amount of nitrates in these waters.

M. M. P. M.

Analytical Chemistry.

Separation of the Alkaline Earths from the Alkalis. By E. Pfeiffer (*Arch. Pharm.* [3], **14**, 52—53).—A weighed quantity of the substance is ignited to remove ammonium salts and water; the residue exhausted with water; and the magnesium precipitated from the solution by baryta-water. On adding ammonia and ammonium carbonate to the filtrate from the precipitate, the excess of the precipitant and any alkaline earths that may be present are thrown down. The filtrate from these carbonates is then concentrated, and from it any dissolved carbonates of the alkaline earths are separated by ammonium oxalate; the filtrate now contains nothing but the alkalis.

E. W. P.

Estimation of Manganese, especially in its Alloys with Iron. By F. Kessler (*Zeitschr. Anal. Chem.*, 1879, 1—14).—The author gives details of improvements on a process published by him in the *Zeitschr.*, **11**, 255; the original method was available to determine manganese up to 13 per cent., but as the percentage of manganese may now reach 90, a modification became requisite.

The solution of iron and manganese as chlorides is slightly oversaturated with sodium carbonate solution (100 grams of crystals to the litre), and hydrochloric acid (1·01 sp. gr.) is then added until the solution just clears. Both these liquids are best run in gradually from burettes. After diluting, sodium sulphate solution (100 grams of crystals to the litre) is added to the cold solution in the proportion of 15 c.c. for each gram of iron; and the whole after being made up to a known volume, is filtered uninterruptedly through a dry filter. Mere traces of iron remain in solution, and do not interfere with the titration of the manganese. From 50 to 150 c.c. of this filtrate, which must not

contain more than 1 decigram of manganese (as previously determined by the estimation of the iron), are then added to a mixture of 100 c.c. of saturated bromine-water with 20 c.c. of sodium acetate solution (500 grams of crystals to the litre), and 50 c.c. of zinc chloride solution (200 grams of zinc to the litre). The solution containing manganese should be added in five nearly equal portions at intervals of a quarter of an hour. Then 20 c.c. more of the above sodium acetate solution are added, and the whole boiled until the smell and colour of bromine have vanished. The precipitate is then rinsed out into a filter, washed with dilute sodium acetate solution (one-fiftieth the strength given above), and the precipitate and filter returned to the precipitation flask. The object of precipitating the manganese in the presence of zinc chloride is to prevent the formation of lower or higher oxygen compounds of manganese.

A solution of antimonious chloride (15 grams of antimonious oxide dissolved in 300 c.c. of hydrochloric acid to the litre) is then added to the precipitate in the flask; it is added 5 c.c. at a time, until, after being well shaken with the precipitate, the latter is no longer black, but brown; 25 c.c. of hydrochloric acid (1·19 sp. gr.) are then added, and as soon as the precipitate is completely dissolved, the whole is rinsed with 200 c.c. of water into a beaker, and titrated with standard permanganate. In this titration the action of antimonious chloride on the permanganate is very rapid, and a colour permanent for six seconds indicates the end of the reaction, even though it may subsequently disappear, from the action of the hydrochloric acid on the permanganate. The solution before titration may be green or yellow from the presence of nickel, copper, cobalt, or iron; of these cobalt alone makes the determination too high by one-half the amount of cobalt present.

The author recommends the use of carefully-prepared pure manganese pyrophosphate for ascertaining the strength of permanganate solution. The salt is prepared by dissolving in water 40 grams of crystallised manganese sulphate, and 60 grams of crystallised sodium phosphate; mixing the solutions, adding hydrochloric acid until clear; then excess of ammonia, again clearing with the acid, filtering, diluting to a litre, and precipitating with ammonia. The precipitate is washed by decantation until it no longer gives the chlorine reaction, and then dissolved in dilute nitric acid, with addition of a little sulphurous acid to reduce manganese sesquioxide; ammonia is added in excess, then nitric acid until clear, and finally excess of ammonia, the precipitate being washed to the same extent as before. This precipitate on ignition gives the pyrophosphate, a portion of which is weighed off after having been recently ignited, dissolved in hydrochloric acid, evaporated over the water-bath, and the water-solution of the residue is titrated with permanganate as directed above. The permanganate solution is made by dissolving the purest salt obtainable, letting the solution become perfectly clear by long standing, and then decanting; it remains unchanged for many months in the dark. Tabulated results of this method are given, which prove its accuracy. Only one specimen of steel—East Indian wootz-steel—was found to be free from manganese. F. C.

Detection of Indican in Urine. By W. Weber (*Arch. Pharm.* [3], **13**, 340—342).—Heller's method for the detection of indican in urine is unsatisfactory, as the presence of small quantities of indican is liable to be masked by other substances present in urine. Schunk's method (*J. pr. Chem.*, **75**, 378) is likewise unsatisfactory. The following is recommended:—30 c.c. of urine are heated (not to boiling) in a cylinder of about 80 c.c. capacity, with an equal bulk of fuming hydrochloric acid, and one or two drops of nitric acid are added. The colour of the mixture darkens, and with much indican assumes a reddish-violet tint. When the liquid is cooled, ether is added, and the whole shaken. When the ether has separated from the aqueous solution, it will be covered with a distinctly blue foam; the ether itself should be of a rose-red or violet colour, whilst the solution below should be coloured brown. The presence of the smallest traces of indican is indicated by the blue colour of the upper layers, from which the indigo-blue gradually separates, and indi-rubin remains dissolved in the ether. E. W. P.

Detection of Salicylic Acid in Beer. By M. Blas (*J. pr. Chem.* [3], **19**, 43—46).—It is found that a quantity of salicylic acid, less than ·075—0·1 gram per litre, when added to beer, cannot be detected with certainty if the ferric chloride reaction be employed, either with the original beer, or after precipitation by lead, or after treatment by animal charcoal. It is much more simple to test for the presence of the acid in the urine voided after drinking the beer, when 0·0012 per cent. can with ease be detected. If 20 c.c. of the urine be examined three hours after the beer has been drunk, it will be found that ferric chloride at first produces a precipitation of phosphates, but after their separation the violet reaction is distinct. For the preservation of light beers, ·05 gram of salicylic acid is sufficient, but 0·2 gram per litre must be added to strong beers; more than this quantity is unadvisable, as a taste is imparted to the beer; the addition of salicylic acid to beer cannot be considered to be an adulteration, as it cannot destroy any of the integral constituents, acting only as a preservative. E. W. P.

Technical Chemistry.

Spongy Iron and Animal Charcoal as Materials for purifying Water. By L. Lewin (*Zeitschr. f. Biologie*, **14**, 483—505).—The greater part of this paper is devoted to an account of experiments on the action of Bischoff's spongy iron filter upon impure water. It is shown that if urine, whether dilute or concentrated, be passed through one of these filters, and if the filter be then washed several times with pure water, the whole or almost the whole of the solid matter, as also of the nitrogen, originally present in the urine, is obtained in the liquid that has passed through the filter. About one-fourth of the total nitrogen of the urine is found in the filtered urine; the first

quantity of wash-water generally contains rather more than a second fourth, and the successive quantities of water contain less and less nitrogen.

Nor is the carbon of organic bodies retained by spongy iron. Almost the whole of the sugar and sodium chloride contained in a quantity of milk serum which was passed through the filter, was proved to be present in the filtered liquid after successive washings with pure water.

Bacteria were also found abundantly in filtered urine which was known to contain these organisms before filtration.

Lead was removed by this filter from a slightly acid solution, but only partially from an alkaline solution; the filtered liquid from which lead had been removed contained considerable quantities of iron.

The author regards the spongy iron filter as merely capable of removing suspended matters, and certainly as not more satisfactory in its purifying action than a common filter of sand.

M. M. P. M.

Carbon Monoxide in Foundry Furnaces. By G. Wolffhügel (*Zeitschr. f. Biologie*, **14**, 506—526).—The greater part of this paper is historical. The author confirms the observations of H. Sainte-Claire Deville and others, to the effect that carbon monoxide diffuses through the heated iron walls of the furnaces in which cast-iron is melted, and is found in the hot air surrounding these furnaces.

A few observations are made on the action of small quantities of carbon monoxide upon the organism. M. M. P. M.

Analysis of Burton Ales and Dublin Porter. By R. Lawrence and C. W. Reilly (*Chem. News*, **38**, 215).—From the following table it will be seen that some of the principal elements of nutrition are present in larger quantities in the foreign and ordinary Dublin double stout than in the Burton ales. The phosphoric acid, which exists in the form of phosphates, was determined in the ash by uranium acetate, whilst in the estimation of the albuminoïd matters, acetic acid, alcohol, and total solids, Jackson and Wonfor's method was used. The quantity of albuminoïd matters was determined by first finding the amount of nitrogen by Will and Varrentrapp's method, and then taking 15·92 parts of nitrogen as equal to 100 parts of albumin. The following numbers express the grains per gallon of the substances estimated:—

	Bass's ale.	Allsopp's ale.	Foreign double stout.	Double stout.	Guinness's single stout.
Albuminoïd matter...	336·8810	321·9548	561·8125	428·708	307·790
Acetic acid	96·0295	167·0500	258·7409	143·150	160·335
Alcohol....	4374·6509	4461·1875	5128·2000	4643·100	3534·300
P_2O_5.....	19·4250	18·3750	123·1100	111·088	82·715
Total solids	4884	3110	4374	5068	3838
Sp. gr.....	1·0138	1·0144	1·01157	—	1·12438

D. B.

General and Physical Chemistry.

Behaviour of Electric Currents in Rarefied Gases. By F. Narr (*Ann. Phys. Chem.* [2], **5**, 145—168).—The author was led by Warburg's experiments (*Pogg.* **145**, 578) to undertake a similar investigation on the electric discharge in rarefied gases. He employed an apparatus essentially similar to that of Warburg, the measuring apparatus, however, being separated from that in which the discharge took place.

His tables show that in all the gases investigated, namely, hydrogen, air, and carbonic anhydride, the intensity of the charge, time being a constant, diminishes with the pressure, that is, with the density of the gas.

When the pressures are equal, the time also being equal, the amount of the charge varies with the nature of the gas, and is greatest with carbonic anhydride and least with hydrogen.

The above-mentioned differences in the charge capable of being estimated by experiment diminish with the pressure, that is, with the densities of the gases, and in a vacuum gradually become smaller than even the errors of manipulation.

The differences in the charge observed take place immediately after the charging of the apparatus, and the further discharge takes place regularly and slowly, and up to the present has not shown sufficient variations for the different gases to lead to any definite results.

In discussing these results, the author comes to the conclusion that the differences in the charges observed are due to differences in the loss of electricity, which must be ascribed to a simultaneous change in the nature and density of the gaseous medium; in fact the loss of electricity which an isolated charged body undergoes in rarefied gases contained in a vessel connected with earth is caused by two processes which differ both in time and in intensity, the first being rapid and short, that is, the discharge, and the second regular and slow, which the author proposes to call the dispersion.

The intensity of the discharge depends therefore on the nature and density of the rarefied gas; and increases in all the gases hitherto investigated as the density diminishes, and also when the latter remains constant in passing from carbonic anhydride to hydrogen. The phenomena described may be attributed, the author thinks, either to the gases themselves and the changes taking place in them, or to extraneous disturbing influences due to the presence of foreign bodies in the dispersion chamber. These substances would be dust, and mercury and water vapours. Warburg thinks that the phenomena may be due to the dust present, but Narr doubts this conclusion.

J. M. T.

Excitation of Electricity by the Contact of Solid and Gaseous Bodies. By W. Beetz (*Ann. Phys. Chem.* [2], **5**, 1—20).—The paper describes determinations of the electro-motive forces of

elements of gas-batteries constructed with various gases, liquids, and solids. The author's general conclusion from his experiments is, that in these combinations the electro-motive forces of gases are not, strictly speaking, the active agents; but rather the differences of electrical tension arising from the contacts of heterogeneous conducting liquids, and the charges induced in the metallic conductors by the occlusion of gases in the substance of the solids, or the adhesion of gases to their surfaces. R. R.

Electrical Currents Produced by the Flow of Liquids through Tubes. By E. Dorn (*Ann. Phys. Chem.* [2], **5**, 20—44).—The author describes in detail his experiments for the investigation of the currents produced by the flow of water through tubes of from 1 mm. to 4·8 mms. diameter. Among the general results which his researches have established or confirmed are the following: For equal velocity of flow, the electro-motive force of the current is proportional to the length of the tube. The electro-motive force depends on the condition of the inner surface of the tube, and varies according to the time during which the tube has remained previously filled with water. It depends also upon the nature of the surface; thus, in a tube coated inside with white wax, a current was observed contrary to the direction of the flow of water.

The simple motion of water will not itself produce an electrical current, which is developed only when the water flows through a tube. R. R.

Deviation of Some Gases from Boyle's Law. By A. Winkelmann (*Ann. Phys. Chem.* [2], **5**, 92—112).—The paper describes at length the author's mode of determining the relations, at 0° and 100° respectively, between the pressures and volumes of gases. The apparatus and methods of experiment were essentially those of Regnault (*Mémoires de l'Academie*, **21**, 341). The subject of research was ethylene, C_2H_4, and the results are summed up in the following empirical formulæ, where V represents the volume of the gas under a pressure of 760 mm. of mercury, and V_P its volume under another pressure, P:

For Ethylene.

$$\text{At } 0^\circ : \frac{V\ 0{\cdot}76}{V_P P} = 1 + {\cdot}008235(P - {\cdot}76) - {\cdot}0006118(P - {\cdot}76)_2.$$

$$\text{At } 100^\circ : \frac{V\ 0{\cdot}76}{V_P P} = 1 + {\cdot}004862(P - {\cdot}76) - {\cdot}00149(P - {\cdot}76)_2.$$

R. R.

Apparatus for Regulating the Atmospheric Pressure in Boiling Point Determinations. By W. Städel and E. Hahn (*Liebig's Annalen*, **195**, 218—221).—By means of this apparatus, the pressure may be either increased or diminished during a distillation without interrupting the operation. The original paper must be consulted for details, as a description of the apparatus could not be understood without the aid of plates. W. C. W.

Diffusion of Carbonic Anhydride through Water and Alcohol. By Stefan (*Chem. Centr.*, 1878, 369).—If carbonic anhydride be enclosed by means of a cylinder of liquid, the gas diffuses through the liquid into the outer air, the amount so diffusing under constant pressure being directly proportional to the surface area of the liquid, and inversely as the length of the cylinder. The sp. gr. of the liquid decreases in regular proportion from the inner layer, which is saturated with carbonic anhydride, to the outer: the amount of carbonic anhydride which diffuses outwards through unit area in unit time is proportional to this decrease in specific gravity, and the factor which expresses this proportion is the coefficient of diffusion. This coefficient may also be determined by allowing the gas to diffuse into a long cylinder of liquid: the amount which so diffuses is proportional to the square root of the time. The diffusion-coefficient of carbonic anhydride into water is nearly equal to that of potassium chloride into water: the diffusion-coefficient of the same gas into alcohol is nearly double that obtained for water. Hydrogen diffuses into liquids more rapidly than any other gas. Mutual action between gas and liquid exerts no influence on the rate of diffusion of the gas into the liquid.

M. M. P. M.

Apparatus for Continual Dialysis. By E. Lebaigne (*Pharm. J. Trans.* [3], **9**, 655).—The apparatus consists of a large flask with faucet at the bottom, full of distilled water; a series of glass funnels, to the short neck of each of which is attached by rubber-tubing a curved syphon passing upwards and over the brim of the next funnel, which is placed at a slightly lower level, the last syphon discharging into a receiving vessel. Each funnel is provided with a plaited filter made of parchment paper, and projecting $\frac{3}{4}$ to $\frac{7}{8}$ inch above the edge of the funnel. The first filter is now charged with solution of chloride of iron (ferric oxychloride) to about three-fourths of its depth. Distilled water is then poured into the funnel and allowed to remain in contact with the filter for twelve hours. Then the second filter is charged in the same manner and the faucet of the flask carefully opened, when the water of the first funnel will be gradually forced over into the second, and will be replaced by fresh distilled water. After twelve hours, another funnel with its filter is connected with the series and this is continued with as many filters as may be desired. The rate at which the distilled water is allowed to pass is controlled by its dropping from the last syphon-tube.

Whenever the contents of the first funnel cease to have an acid reaction, and to be precipitated by silver nitrate, they are withdrawn, the second filter is made the first, and a new funnel with filter inserted at the end.

The proportions adopted for making dialysed iron are the fol lowing:—

Solution of ammonia, sp. gr. '920	400 parts.
Distilled water	400 ,,
Solution of ferric chloride, sp. gr. 1'260 ..	1000 ,,

Mix the distilled water and ammonia, and add the mixture gradually

to the solution of ferric chloride, under constant stirring, until a clear mixture is produced.

Experience having shown that among crystalloïds, chloride of sodium dialyses best, it is thought that it would perhaps be an advantage to replace the ammonia by soda or sodium carbonate. E. W. P.

Dissociation of Dissolved Ferric Salts. By G. Wiedemann (*Ann. Phys. Chem.* [2], **5**, 45—83).—The method of investigation described in this paper consists in observing the magnetism of various salts of iron and other substances in the dissolved state, the solvents being water, alcohol, or acids. The liquid is contained in a small glass vessel attached to an arm of a torsion-balance, the deflections of which are indicated by the degree of a scale reflected in a mirror. The pole of a powerful electro-magnet is placed near the bulb containing the magnetic liquid, whose chemical constitution is inferred from the deflection, the magnetic effect of the several ingredients or compounds concerned having been determined by previous experiments. The author claims for this method the amount of accuracy necessary to determine quantitatively the chemical constitution of liquids containing salts of the magnetic metals; and he refers to other cases in which the chemical constitution of a substance may be inferred from physical data, such as optical or calorimetric measurements. The author's results as to the constitution of solutions of iron salts under certain conditions are given in the original paper.

R. R.

Chemical Affinity. By W. Oswald (*J. pr. Chem.* [2], **18**, 328—371).—In this paper the author endeavours to arrive at the relative affinities of different acids by comparing the changes of volume which take place when solutions of the acids are neutralised with potash, soda, and ammonia. His method of experimenting was as follows:—Solutions of the acids and bases (the latter perfectly free from carbonic acid) were prepared of such a strength that one equivalent in grams was contained in 1,000 grams of solution, and the specific volume of each was accurately determined by the pycnometer. Equivalent quantities of each acid and base were then mixed together; the specific volumes of the saline solutions thereby produced were determined as before, and the resulting expansion or contraction thus measured. For example, the specific volume of a solution of nitric acid containing one equivalent (in grams) of the pure acid in 1,000 grams of solution was found to be ·966623. Similarly, the specific volume of a solution of potash containing one equivalent (in grams) of pure potash in 1,000 grams of solution was found to be ·950668. When equivalent quantities of these two solutions were mixed together it was found that the specific volume of the solution of potassium nitrate produced was ·968673. In other words, the solution of potassium nitrate formed by mixing 966·623 vols. of the nitric acid solution with 950·668 vols. of the potash solution was found to measure 1,937·337 vols., showing an increase of 20·046. The following table contains the corresponding results obtained with other acids and bases, the positive sign prefixed to the numbers indicating increase,

and the negative sign diminution in the volume of the saline solution formed.

The table contains also a series of numbers in brackets, which represent the differences between the sums of the coefficients of refraction of the acids and bases determined separately, and the coefficient of refraction of the saline solutions formed on mixing them. Thus, the coefficient of refraction of the nitric acid solution (multiplied by 100,000 for convenience) was found to be 134,076 and that of the potash solution 134,357, whilst that of the potassium nitrate solution produced by mixing them in equivalent proportions was 267,536 (134,076 + 134,357 − 267,536 = 897). In the table, the negative sign indicates a reduction, and the positive sign an increase in the coefficient of refraction. The determinations were made at the temperature of 20°, sodium-light being employed.

Acids.	Potash.		Soda.		Ammonia.	
Nitric	+ 20·046	[− 897]	+ 19·770	[− 888]	− 6·441	[+ 139]
Hydrochloric	+ 19·521	[− 882]	+ 19·238	[− 879]	− 6·572	[+ 148]
Hydrobromic	+ 19·626	[− 916]	+ 19·336	[− 907]	− 6·565	[+ 117]
Hydriodic	+ 19·799	[− 938]	+ 19·535	[− 923]	− 6·442	[+ 100]
Formic	+ 12·361	[− 484]	+ 12·153	[− 478]	− 13·593	[+ 536]
Acetic	+ 9·522	[− 363]	+ 9·287	[− 354]	− 16·261	[+ 646]
Monochloracetic ..	+ 10·855	[− 425]	+ 10·628	[− 412]	− 15·087	[+ 603]
Dichloracetic	+ 12·946	[− 552]	+ 12·702	[− 544]	− 12·975	[+ 473]
Trichloracetic	+ 17·357	[− 774]	+ 17·067	[− 774]	− 8·665	[+ 264]
Propionic.....	+ 7·830	[− 318]	+ 7·679	[− 306]	− 17·822	[+ 699]
Butyric	+ 6·984	[− 279]	+ 6·844	[− 269]	− 18·633	[+ 730]
Isobutyric	+ 6·301	[− 254]	+ 6·174	[− 248]	− 19·270	[+ 758]
Glycollic	+ 9·616	—	+ 9·517	—	− 16·496	—
Lactic	+ 8·267	[− 353]	+ 8·133	[− 344]	− 17·739	[+ 661]

With regard to the numbers relating to *volume* in the above table, the author points out that the difference between the numbers found for any two bases is nearly constant throughout the series of acids. The difference between potash and ammonia for instance is about 26 all through the table, and the differences between soda and ammonia, and between potash and soda are equally constant. He points out further that the differences between the numbers arrived at for any two acids are approximately the same in the three columns of bases. This constancy of difference in both the horizontal and vertical series of numbers is shown to be a necessary consequence of the hypothesis that *the change in physical properties due to chemical combination is of constant value for each substance entering into combination, and is therefore independent of the other substances combining with the first.**

With respect to the numbers in brackets in the above table, the author points out that the differences in refraction follow those of

[* This is the literal rendering of the author's words. The idea would be better expressed by saying that *in chemical combination the alteration of physical properties due to any one substance entering into combination is of constant value, and is independent of the alteration due to other substances.*—J. R.]

volume (with opposite signs), although the two sets of numbers are not strictly proportional.

Another set of experiments made by the author consists in adding an equivalent of a free acid to the normal salt of another acid, and determining the alteration of volume thereby produced. At the same time the effect of adding a free acid to a normal salt of the same acid was determined, the numbers thus found being, however, very small and unimportant. From the three sets of numbers thus obtained, he calculates the proportion in which a base divides itself between equivalent quantities of two acids. The results are given in the following table, where the first column contains the names of the normal salt and of the free acid added, and the numbers in the four last columns show the percentage of base taken up by the added acid. These numbers were arrived at by dividing the alteration of volume due to the action of free acid on the salt by the difference between the volume-changes due to the neutralisation of the base by the two acids separately, a small correction being made for the effect of a free acid on its normal salts.

	Potash.	Soda.	Ammonia.	Mean.
Dichloracetate : Nitric	77	77	75	76
Dichloracetate : Hydrochloric	74	75	73	74
Dichloracetate : Trichloracetic	71	71	71	71
Dichloracetate : Lactic	8	9	11	9
Monochloracetate : Trichloracetic	92	92	92	92
Formate : Trichloracetic	97	96	97	97
Formate : Lactic	43	46	48	46
Formate : Acetic	25	23	23	24
Formate : Butyric	21	21	19	20
Formate : Isobutyric	19	19	18	19
Butyrate : Acetic	54	52	53	53
Isobutyrate : Acetic	56	51	53	53
Propionate : Formic	78	80	79	79
Glycollate : Formic	43	44	45	44

The experiments of Thomsen (*Pogg. Ann.*, **138**, 65) and of the author have shown that the affinities of nitric and hydrochloric acids are nearly equal, being in the proportion of 100 : 98. Taking these numbers as starting-points, the author calculates the relative affinities of other acids on the above table thus:—Nitric acid = 100, dichloracetic acid = $\frac{24}{76} \times 100 = 32$; hydrochloric acid = 98, dichloracetic acid = $\frac{26}{74} \times 98 = 34$; whence follows dichloracetic acid (mean) = 33, trichloracetic acid = $\frac{71}{29} \times 33 = 80$, lactic acid = $\frac{9}{91} \times 33 = 3{\cdot}3$, and so on through the table. The final results are as follows:—

Relative Affinities.

Nitric acid	100	Formic acid	3·9
Hydrochloric acid	98	Lactic „	3·3
Trichloracetic „	80	Acetic „	1·23
Dichloracetic „	33	Propionic acid	1·04
Monochloracetic acid	7	Butyric „	0·98
Glycollic acid	5	Isobutyric acid	0·92

Similar experiments with succinic, malic, and tartaric acids led to the numbers 1·45, 2·82, and 5·2 respectively.

The author remarks that the numbers here given are very uncertain, but he believes that the *order* of the acids will not be materially affected by more exact determinations.

The effect of chlorine in increasing affinity is shown in a remarkable manner in the three derivatives of acetic acid. A similar increase of affinity is brought about by oxygen, as shown in the differences between acetic and glycollic, and between propionic and lactic acids. On the other hand, affinity is reduced by addition of CH_2, as seen in the series of acids from formic to butyric, and also in glycollic and lactic acids. J. R.

Relative Affinities and Reciprocal Displacements of Oxygen and the Halogen Elements. By Berthelot (*Ann. Chem. Phys.* [3], **15**, 185—220).—The author in this paper shows that the reciprocal displacements between the halogens and oxygen may be foreseen from the quantities of heat disengaged in the formation of the compounds which the metal and the metalloïds form with oxygen on the one hand and with the halogens on the other. His demonstration of this point is partly based on the comparison of already well known numerical data, and partly derived from the measurement of thermic quantities not before determined, such as the heat evolved in the formation of the bromides and iodides of aluminium, tin, arsenic, &c. He has investigated more particularly in this paper the reactions of—

1. Metals forming salifiable bases, properly so called,
2. Aluminium,
3. Tin,
4. Phosphorus and arsenic,
5. Silicon and boron,

the paper giving full details of the numerical results obtained for these bodies.

The author finds that the comparative reactions of the halogen elements and oxygen on these different bodies, and the reciprocal displacements of iodine and oxygen in particular, depend neither on the type nor on the atomic or other formula of the compounds, but that they do depend on the quantities of heat disengaged by the direct combination of the metals with each of the elements taken in equivalent weights, these quantities of heat being, he considers, capable of indicating the direction, peculiarities, and even inversion of the reactions.

His observations are further supported by previous investigations on—

The reciprocal displacements between water and the hydracids contrasted with metallic oxides (*ibid.* [5], **6**, 303).

Between hydric sulphide and the hydracids opposed to metallic sulphides (*ibid.* [5], **6**, 186, 194, 198, and 494).

Between cyanhydric acid and the hydracids opposed to metallic cyanides (*ibid.* [4], **30**, 494).

Between hydrochloric, hydrobromic, and hydriodic acids and metallic chlorides, bromides, and iodides (*ibid.* [5], **4**, 500 and 506).

Between the halogens and their respective hydracids (*ibid.* [5], **6**, 300; **4**, 59 and 506).

Between potassium oxide and silver oxide opposed to hydrochloric acid (*ibid.*, 536).

Between sulphuric acid and hydrochloric or nitric acid in their dissolved salts (*ibid.* [4], **30**, 514).

Between hydriodic and sulphydric acids opposed to iodine and sulphur, and between hydriodic and sulphurous acids opposed respectively to each other (*ibid.* [5], **4**, 495 and 498).

The author considers that he has thus been enabled to connect a series of hitherto disconnected and partially unexplained empirical results by a clear and precise theory. This theory deduces the reciprocal action of the compounds on each other and on their elements from the quantities of heat developed in the formation of each compound, provided that the conditions of existence of the compound in the free state be known, as also the degree of stability or dissociation peculiar to it at different temperatures and in different media; that is to say, the exact conditions under which it pre-exists or is to be found during the reaction. J. M. T.

Preparation of large regular Crystals. By F. Meyer (*Arch. Pharm.* [3], **13**, 342—345).—A solution is made of the salt of which a large crystal is desired, so concentrated that a portion crystallises out after 24 hours' standing. A well-formed crystal is picked out and laid on a glass plate, which is again placed in a glass dish; upon this is poured the mother-liquor, to which a small quantity of fresh salt has been added, and the whole left in a cool place of even temperature. This treatment is repeated every 12—14 hours until the crystal has acquired the desired size. The solution should not be too concentrated, as the crystal is liable to grow irregularly; if this happens it must be turned over on the plate, and small adherent irregularities should be removed. By regulating the position of the crystals definite faces can be made to increase. By this process a chrome-alum crystal has been coated with ordinary alum, the whole crystal weighing 3 lbs. E. W. P.

Inorganic Chemistry.

Reactions of Iodine and of Potassium Iodide with Sulphurous Acid. By A. E. Menke (*Chem. News*, **39**, 19).—Hydriodic acid and sulphurous acid in aqueous solution form a yellow liquid from which sulphur eventually separates (Saladin, *J. Chim. Med.*, **7**, 528). The author concluded that the yellow colour given by potassium iodide with sulphurous acid was due to the action of the latter on the hydriodic acid set free, and was anxious to isolate the substance produced. Carbon bisulphide removes no free iodine from the solution, but on agitation with ether and a little alcohol, a pungent oily brown fluid is removed, which evolves iodine when heated. If iodine be dissolved in alcohol, and sulphurous anhydride passed in to saturation, the

liquid becomes dark, but is decolorised by water. If sulphurous anhydride be again passed in until no more free iodine is present, a yellow plastic substance is deposited after standing, which appears to be a sulphide of iodine. The author suggests that the reactions are as follows:—

(1.) $KI + H_2SO_3 = HI + KHSO_3$.
(2.) $8HI + 2SO_2 = 4H_2O + I_6 + I_2S_2$ (?).
(3.) $I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4$.

E. W. P.

Action of Potassium Permanganate on Oxalic Acid. By A. R. Leeds (*Chem. News*, **39**, 18).—In a former paper (*ibid.*, **38**, 224) the author stated his belief that a mixture of oxalic acid and potassium permanganate liberated ozone in the presence of water; but he has since made experiments which tend to show that the former conclusions were erroneous.

Further experiments were deemed necessary to settle the question, and for that purpose 25 grams of pulverised permanganate were introduced into a half-liter flask, provided with a funnel and stop-cock, and sulphuric acid run in through the funnel drop by drop. The escaping gas, after passing through a wash-bottle, traversed a Geissler's absorption apparatus containing potassium iodide. No iodine was set free, but chlorine was found in the wash-bottle. This led to the examination of the permanganate and oxalic acid, and it was found that there was chlorine in the oxalic acid, and that the permanganate contained 0·148 per cent. of chlorate.

The results show that no ozone is produced as at first supposed, but that the reactions observed are due to chlorine. E. W. P.

Hydrogen Peroxide. By E. Schöne (*Liebig's Annalen*, **195**, 228—252).—Hydrogen peroxide liberates iodine from pure potassium iodide; oxygen is evolved, and the solution acquires an alkaline reaction, which is due to the formation of caustic potash. The action of the potassium iodide on the peroxide is catalytic, a minute quantity of potassium iodide being able to decompose a relatively large quantity of hydrogen peroxide. As the solution is diluted the reaction begins later and proceeds more slowly.

The following changes are supposed to occur. A portion of the potassium iodide dissociates when dissolved in water, and the hydrogen peroxide attacks both the caustic potash and the hydriodic acid.

1. $2KI + 2H_2O = 2KHO + 2HI$.
2. $H_2O_2 + 2KHO = K_2O_2 + 2H_2O$.
3. $H_2O_2 + 2HI = I_2 + 2H_2O$.
4. $K_2O_2 + I_2 = 2KI + O_2$.

The regenerated potassium iodide is then able to decompose another molecule of hydrogen peroxide.

Alkaline chlorides and bromides also decompose hydrogen peroxide, but the halogens are not liberated, and the liquid does not become alkaline. A hypochlorite or hypobromite is probably formed, which decomposes the peroxide, as shown by the following equation:— $KClO + H_2O_2 = KCl + H_2O + O_2$. W. C. W.

Experiments on the Preparation of Sulphuric Bromide and Sulphur Oxytetrabromide. By F. Clausnizer (*Deut. Chem. Ges. Ber.*, **11**, 2012—2013).—Attempts to prepare sulphuric monobromide, $SO_2(OH)Br$, by the action of hydrobromic acid on sulphuric anhydride, or by adding phosphorus pentabromide to sulphuric acid, were unsuccessful. Sulphur oxytetrabromide could not be obtained by the action of sulphuric anhydride on a solution of sulphur in bromine.

W. C. W.

Composition of Commercial Ammonium Carbonate and of the Product formed on exposing it to Air. By H. Vogler (*Zeit. Anal. Chem.*, 1878, 451—455).—The analyses of commercial ammonium carbonate have hitherto yielded discordant results, and the water it contains has never been directly estimated. The author, after carefully breaking away the outer portions of a large piece of the white crystalline transparent ammonium carbonate, determined the carbonic acid in the central portion by liberating it with sulphuric acid and absorbing it with soda-lime, and the ammonia by dissolving in excess of standard sulphuric acid and determining the excess by standard soda-solution. The total hydrogen was then estimated by combustion with copper oxide in presence of much metallic copper carefully freed from hydrogen. To avoid oxidation of the copper, the process was conducted in a slow stream of carbonic acid. The hydrogen present as ammonia was subtracted from the total hydrogen, and the residual hydrogen calculated as water. The formula arrived at was $NH_4HCO_3 + 2(NH_3.CO_2)$.

Some of the unaltered ammonium carbonate in the state of powder was then inclosed over strong sulphuric acid and slaked lime: it lost in fifteen days about one-tenth of its weight. The carbonic anhydride and ammonia were directly estimated in the product thus obtained, the water was calculated by difference. The composition of the substance was found to be represented very nearly by the formula NH_4HCO_3. This substance volatilises very freely when exposed to the air; it is odourless, but produces an ammoniacal smell by decomposition on exposure to the air.

F. C.

Atomic Weight of Antimony. By R. Schneider (*Ann. Phys. Chem.* [2], **5**, 265—281).—The author was led as early as 1856 to doubt the accuracy of Berzelius's determination of 129 as the atomic weight of antimony. In his paper, published in *Pogg.*, **98**, 293, he has explained his reasons for using a natural instead of an artificial compound of that body for his investigations, the mineral chosen being a remarkably pure antimony glance. The method he then employed was the direct reduction of the glance in pure hydrogen, and he now calls attention to the fact that Dumas' objection to this process, on account of the volatilisation of antimony sulphide, cannot be considered of any consequence: for if the current of hydrogen is kept constant and slow, and the sulphide is not heated more strongly than necessary for the reduction, and a proper tube is employed, only traces of the sulphide are volatilised, the largest quantity volatilised in his experiments being ·002 gram when 10·5 grams of substance were used. Small quantities of sulphur retained in the molten antimony

were determined as barium sulphate. The average of eight experiments conducted as described in the paper mentioned above gave him, as the atomic weight the number 120·3, which agrees fairly with H. Rose's determination of 120·64. Dexter in 1857 determined it from small quantities of pure antimony as 122·33, and Dumas, by the precipitation of antimony chloride by a silver solution, obtained the number 121·97. The authority of Dumas' name, and the close agreement of his figures with those of Dexter, having led to its universal adoption, Schneider at that time called attention to the inaccuracy of the method employed, and to show the justice of his criticism he now brings forward the late experiments of H. P. Cook (*Sill. Amer. Jour.* [3], **15**).

This latter author made his principal determinations by precipitating antimony as sulphide from a tartaric acid solution, and weighing it both as the red modification first obtained and then in the black modification obtained from the former by heating to 210°. From the first series, thirteen in number, he obtained 119·994, and from a second series, eleven in number, 120·295 as the atomic weight. Schneider gives a long and careful criticism of the results so obtained, pointing out that in Cook's own words, "the best determination and as perfect as could be made under the conditions" give the atomic weight of Sb as 120·14. Mr. Cook was naturally much struck with the difference between his own and the author's results, and those of Dumas; he therefore carefully repeated Dumas' experiments, and obtained the number 121·94 (122·33 Dumas). This naturally led Mr. Cook to make a large series of observations on the halogen compounds of antimony, the result of which is that he concludes Dumas' error to be due to the presence of a small quantity of oxygen in the salt due to the hygroscopic nature of antimony chloride. Schneider concludes his paper by pointing out that as early as 1859 he himself had called attention to this fact, which has been confirmed by Cook's recent experiments. J. M. T.

Some Bismuth Residues. By E. A. Letts (*Pharm. J. Trans.* [3], **9**, 405—407).—The examination of a residue obtained when commercial bismuth was treated with nitric acid showed that bismuth, gold, silver, tellurium, selenium, and a trace of copper were present. The residue probably consists of a mixture of tellurides and selenides of bismuth, gold, and silver; tellurium is present to the amount of at least 12 per cent., silver 5 per cent., bismuth about 44 per cent., and gold to about 2 per cent. Great difficulty was experienced in separating selenium from tellurium, owing to the inaccuracy of the cyanide method, unless performed with special precautions as regards temperature of fusion, and filtration of the solution of the fused mass in an inactive atmosphere. E. W. P.

Tungstates of the Earthy and Metallic Sesquioxides. By J. Lefort (*Compt. rend.*, **87**, 748—751, and *Ann. Chim. Phys.* [5], **15**, 321—362).—It has been shown that by the action of acetic acid at different temperatures on the neutral sodium and potassium tungstates, three definite tungstates can be isolated, viz., $2(WO_3)M_2O$; $3(WO_3)M_2O$;

$5(WO_3)2M_2O$, so that starting from a neutral tungstate the following series of compounds may be obtained :—$WO_3.M_2O$, normal tungstate; $2(WO_3)M_2O$, ditungstate; $3(WO_3)M_2O$, tritungstate; $4(WO_3)M_2O$, tetra- or meta-tungstate; $5(WO_3)2M_2O$, penta- or intermediate tungstate, so called because it may be regarded as a double tungstate representing a di- and tri-tungstate, thus, $5(WO_3)2M_2O = 2(WO_3)M_2O + 3(WO_3)M_2O$.

In the tungstates of monoxides or bases containing one atom of oxygen (with the exception of mercury) the ratio of acid to base is as 1 to 1 for the neutral salts, and as 2 to 1 for the acid salts; in the case of tungstates of the sesquioxides, the proportions of acid and base vary with almost every metal, the salts containing sometimes an excess of acid and sometimes an excess of base.

Aluminium Tungstates.—The neutral salt is prepared by mixing solutions of alum and sodium tungstate; it forms a white voluminous precipitate, soluble in 1,500 parts of water.

The acid salt closely resembles the preceding, and is made by substituting acid sodium tungstate for the neutral salt. It is soluble in 400 parts of water at 15°.

Iron Tungstates.—Ferrous acetate precipitated by the neutral or by the acid sodium tungstate produces an unstable salt which could not be obtained in a condition fit for analysis; but ferric acetate under similar circumstances produced yellowish precipitates which were perfectly definite. The neutral tungstate dissolved in 300 parts of water, and the acid salt in 50 parts at 15°.

Chromium Tungstates.—A greenish-blue basic tungstate was thrown down by the addition of neutral sodium tungstate to chromium acetate, soluble in 400 parts of water; but the neutral tungstate was obtained by the substitution of chrome alum for the acetate. The latter precipitate was of a dirty green colour, and very slightly soluble in cold water.

The acid salt was prepared by mixing solutions of acid sodium tungstate and chromium acetate, and pouring the mixture into concentrated alcohol; the deep green deposit thus obtained is decomposed by water, a greenish-white powder resulting, which is the salt in question. It is soluble in 50 parts of cold water.

Uranium Tungstates.—Uranium acetate and neutral sodium tungstate produce a yellow amorphous precipitate, which is not neutral, but basic. The neutral salt is produced by precipitating the acetate with acid sodium tungstate. The basic tungstate is much less soluble in water than the neutral salt.

Antimony Tungstates.—A solution of tartar emetic poured into a solution of neutral sodium tungstate produces after some minutes a heavy white precipitate, which is probably the neutral antimony tungstate. It is, however, decomposed by water, so that a satisfactory analysis could not be obtained. The acid tungstate, on the contrary, is stable, and appreciably soluble in water without decomposition.

Bismuth Tungstates.—By precipitating solutions of bismuth nitrate as in the previous instances, insoluble bismuth tungstate was obtained, which was rapidly decomposed by water into acid and basic salt. The acid tungstate, however, crystallised from very concentrated solutions

containing sodium acetate in the form of white micaceous scales, which seemed definite as far as could be judged from their appearance. They could not be purified without undergoing decomposition, and an approximate analysis only was effected.

The following tungstates have been prepared, examined, and analysed:—

Barium tungstates.....	$BaWO_4$; $BaO.2(WO_3).H_2O$.
Strontium tungstates...	$SrWO_4$; $SrO_2(WO_3).3H_2O$.
Calcium tungstates	$CaWO_4$; $CaO.2(WO_3)$; $CaO.2(WO_3).H_2O$.
Magnesium tungstates ..	$MgWO_4.3H_2O$; $MgO.2(WO_3).8H_2O$.
Aluminium tungstates ..	$Al_23(WO_4).8H_2O$; $Al_2O_34(WO_3).9H_2O$.
Manganese tungstates ..	$MnWO_4.H_2O$; $MnO.2(WO_3).3H_2O$.
Ferric tungstates	$2(Fe_2O_3)3(WO_3).6H_2O$; $Fe_2O_32(WO_3).4H_2O$.
Chromium tungstates ..	$Cr_2O_32(WO_3).5H_2O$; $Cr_23(WO_4).3H_2O$; $Cr_2O_34(WO_3).6H_2O$.
Nickel tungstates	$NiWO_4.5H_2O$; $NiO2(WO_3).5H_2O$.
Cobalt tungstates	$COWO_4.2H_2O$; $CoO2(WO_3).5H_2O$; $CoO2(WO_3).8H_2O$.
Uranium tungstates	$U_2WO_6.2H_2O$; $U_23(WO_4).5H_2O$.
Zinc tungstates	$ZnWO_4.H_2O$; $ZnO2(WO_3).3H_2O$.
Cadmium tungstates	$CdWO_4$; $CdO2(WO_3).3H_2O$.
Antimony tungstate	$Sb_2O_35(WO_3).4H_2O$.
Bismuth tungstate.....	$Bi_2O_36(WO_3).8H_2O$?
Lead tungstates	$PbWO_4$; $PbO2(WO_3).2H_2O$.
Copper tungstates	$CuWO_4.2H_2O$; $CuO2(WO_3).5H_2O$.
Mercury tungstates	$HgWO_4$; $3(HgO)5(WO_3).5H_2O$; $HgO3(WO_3).7H_2O$.
Silver tungstates.....	$Ag_2WO_4.Ag_2O.2(WO_3).H_2O$. J. W.

Mineralogical Chemistry.

Composition of the Gas which issued from one of the Shafts of Abercarn Colliery. By J. W. Thomas (*Chem. News*, **39**, 27).—The gas which was analysed was collected from one of the shafts of the above colliery, ten days after the explosion, in September, 1878. At the time of collection it was issuing at the rate of 500 c. ft. per minute; a fortnight later the second collection (II) was made, when the gas was issuing at the rate of 1,200 c. ft. per minute:—

Composition of the Gas in 100 *Parts.*

	No. I.	No. II.
Carbonic anhydride	2·54	2·43
Air { Oxygen	2·73	none
Air { Nitrogen	10·32	—
Marsh-gas	49·11	74·63
Hydride of ethyl.....	0·95	0·81
Nitrogen	34·35	22·13
	100·00	100·00

The absence of carbonic oxide in I is probably due to the fact that there was a plentiful supply of air before the flooding of the colliery; No. II doubtless consists of a mixture of blower gases, and the gases evolved from exposed coal. The nitrogen probably escaped from the coal under ordinary conditions in the same way as it does in a vacuum. E. W. P.

Natural Crystals of Magnesium Sulphate (Epsomite) of Large Size. By P. de Rouville (*Compt. rend.*, **87**, 703).—Natural crystals of magnesium sulphate, of more than 1 centimeter in length, were found coating the walls of a gypsum quarry in the department of Hérault. The sulphate was in a constant state of exudation, and as it crystallised formed a lustrous coating over the gypsum. No explanation is given of its origin, but the rapidity of its formation and the size of its crystals render it rather an interesting mineralogical phenomenon. J. W.

Crystal System of Tridymite. By A. Lasaulx (*Jahrb. f. Min.*, 1878, 408—409).—The author has discovered that tridymite crystallises in the rhombic system, and not in the hexagonal system, as stated by vom Rath. The crystals exhibit a hexagonal pseudosymmetry, the apparently simple hexagonal plates being in reality twins resembling those of aragonite. It is probable that the asmanite of Maskelyne and tridymite are identical, and are isomorphous with brookite, which, like arkansite, exhibits a hexagonal pseudosymmetry. C. A. B.

Milarite. By E. Ludwig (*Jahrb. f. Min.*, 1878, 411).—Former analyses of this mineral differed so greatly, that Ludwig considered it desirable to make a new analysis. The results are as follows, viz.:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	H_2O.
71·81	10·67	11·65	4·86	1·36 = 100·35,

from which the formula $Si_{12}Al_2Ca_2KHO_{30}$ is deduced. Tschermak determined the physical properties of milarite, and found each crystal to be built up of at least six individuals, which are united together in three different directions, at about 120°; consequently the crystals resemble the trilling crystals of aragonite and witherite. The twin-plane is ∞P, and all the results obtained by Tschermak showed that milarite is rhombic, and not hexagonal. C. A. B.

Production of Felspars by Fusion, and by Prolonged Maintenance at a Temperature near that of Fusion. By F. Fouqué and M. Lévy (*Compt. rend.*, **87**, 700—702).—Natural porphyritic felspars, and artificial mixtures of the elements composing them, were fused in platinum crucibles, at a temperature near the melting point of platinum, until a homogeneous fluid mass was obtained. The crucible was then quickly brought over a gas blowpipe, and maintained for 48 hours at a temperature as little as possible below the original fusing point of the substance. The whole was then allowed to cool without any special precaution. During the heating over the blowpipe, the fused mass generally swelled up, and acquired a porcelain-

like appearance; an examination with the polarising microscope at this stage, of thin plates sawn from different layers, showed distinctly that the artificial felspars had assumed a crystalline structure throughout. In this manner, crystalline masses of oligoclase, labradorite, and albite were obtained, in which the structure and contained crystals were easily recognisable, and capable of being compared with those of natural specimens. In some cases the temperature employed for fusion was not the most favourable for the crystallisation of the mineral, and then smaller and less numerous crystals were obtained; it seldom happened, however, that the latter were not sufficiently well characterised to be recognised, or were too small to permit of their optical properties being studied.

Since felspars crystallise with such facility, even on the small scale, it seems surprising that artificial specimens have not been examined before; it would appear to be due to the want of employment of the microscope, and to the uncertainty which for a long time prevailed respecting the optical properties of these minerals when examined with polarised light; at the same time the easy crystallisation of felspars might have been predicted, having regard to their abundance in eruptive rocks, and to the very varied conditions under which they are not unfrequently found.

The authors propose to continue their research, with a view of reproducing not merely simple felspars, but also associations of different minerals, containing, if possible, constituents which are volatile under ordinary conditions. J. W.

Artificial Crystallisation of Orthose. By St. Meunier (*Compt. rend.*, **87**, 737—738).—In a manner somewhat similar to that of MM. Fouqué and Lévy mentioned in the preceding paper, the author has succeeded in obtaining artificially crystallised orthose; not, however, by starting from the felspar properly so called, but by submitting to devitrification the natural vitreous masses known as *retinites*.

The retinite, placed in a crucible, was brought to fusion and maintained at that temperature for about 36 hours. At the end of that time, it presented the appearance of a clear grey glass, which on being allowed to remain for eight days at a temperature favourable to devitrification, became slowly filled with groups or bundles of crystals. The latter on analysis were found to correspond in composition with orthose, and when cut in thin plates to act energetically on polarised light, colouring the ray strongly at the same time.

An experiment conducted with 1 kilogram of material confirmed the preceding results, whilst another, also on the large scale, furnished an artificial mineral apparently intermediate between retinite and porphyry. J. W.

Adular from Verespatak. By A. Koch (*Jahrb. f. Min.*, 1878, 408).—The occurrence of adular in metallic veins is unusual, particularly in company with gold. The matrix is trachyte, enclosing a large pyramidal quartz crystal, and one face is covered with a vein 4 mm. in thickness, filled up with the following minerals: rock-crystal, milk-white adular, arborescent and crystallised gold, and cubical

crystals of iron-pyrites. The adular crystals exhibit the combination $\infty P . P\infty . 0P . \infty R \infty$, with a peculiar growth in rows parallel to $\infty P\infty$.

C. A. B.

Saccharite. By A. v. Lasaulx (*Jahrb. f. Min.*, 1878, 623).—In 1845 Glocker described (*Journ. f. prakt. Chem.*, 1845, **34**, 494) a mineral which he named saccharite, from its granular, sugar-like appearance. It was originally found on the Gläsendorfer Berg, near Frankenstein, in Saxony, in a chrysoprase mine. According to Glocker, saccharite incloses pinchbeck-brown mica-scales, small plates of talc, green fibrous hornblende, long isolated tourmaline crystals, and finely divided disseminated iron pyrites, the surface of the specimens being generally coated with a crust of green pimelite. According to an analysis by C. Schmidt (*Pogg. Ann.*, 1841, **52**, 473), saccharite is a felspar most nearly approaching andesine in composition. The author obtained some specimens of a mineral (which appeared to be identical with saccharite in its physical properties) from the five serpentine mounds of the Gumberg, near Frankenstein, and examined them microscopically, together with the original specimen described by Glocker. Glocker's saccharite consists mostly of a fine-grained mixture of plagioclase, exhibiting a very distinct twin-striation, and optical properties closely resembling those of oligoclase or andesine. Orthoclase occurs next in amount after the plagioclase, then hornblende and tourmaline crystals, whilst in one specimen (in addition to the minerals already mentioned) minute fibres of talc were observed. Some specimens of saccharite from the Wachberg, near Baumgarten, contained a large quantity of round quartz grains, together with plagioclase, and a few isolated epidote grains. The Gumberg saccharite differs considerably in its microscopical character from that of the other localities, although its outward appearance is almost identical with that of Glocker's saccharite, some specimens being white, with a green coating of pimelite, whilst others have a yellowish, reddish, and intensely red colour. Quartz was found to be the predominating constituent of Gumberg saccharite. The yellowish-red specimens were found to be a mixture of predominating quartz, with a small quantity of plagioclase, and a small quantity of colourless, granular garnet, diopside, and epidote. The garnet grains are generally arranged in rows, one behind the other, but they occur sometimes in bands and lenticular forms, in conjunction with granular quartz-aggregates. They seldom inclose other minerals, quartz being the only exception. The brown-red saccharite owes its colour to ferric oxide, which is evenly distributed throughout the mass. The felspar grains did not exhibit any signs of decomposition in any of the specimens, a fact which is at variance with the opinion that "saccharite is a felspar very much altered, and undergoing decomposition" (*Blum. Min. Q. Aufl.*, 310). From microscopical examination of the various varieties of saccharite, the author is of opinion that it cannot any longer be considered as a distinct plagioclase species, but only as a rock-like varying mixture of plagioclase with other minerals, because the plagioclase almost disappears in some cases, and he concludes from its peculiar occurrence in the serpentine rocks, that it is a product of the decomposition of hornblende rocks.

C. A. B.

Garnet, from the Erratic Gneiss of Wellen, near Bremen. By O. Land (*Jahrb. f. Min.*, 1878, 410).—This garnet is characterised by a peculiar distortion, which gives it a prismatic "habit." It is found in granular gneiss, which is characterised by the absence of plagioclase. The porphyritic structure of this gneiss is caused by the embedded garnets, whilst the prismatic development of the enclosed accessory minerals is caused by the influence of the parallel structure of the gneiss, this influence being exerted even upon microscopical enclosures, for instance, upon innumerable colourless acicular microlites enclosed in the garnets. These microlites are grouped into sheaves and bundles, and have arranged themselves in a direction parallel to the direction of distortion of the garnets. The author could not ascertain to what mineral species the microlites belonged.

C. A. B.

Chromium-Garnet in Silesia. By Klien (*Jahrb. f. Min.*, 1878, 411).—This mineral is found at Jordansmühl as a green deposit upon prehnite, the rhombic dodecahedron being recognizable. It is accompanied by chrome-iron-ore, and no doubt owes it origin to this mineral. C. A. B.

Catlinite. By Klien (*Jahrb. f. Min.*, 1878, 405).—This mineral is found in Rocky County, South Minnesota. It has a brick-red colour, with a bluish tinge, and was named catlinite by Jackson, after the American traveller Catlin. Jackson considered it to be a definite species and described it as a sodium-aluminium silicate, but Dana considered it to be a rock-mass (felsart), and not a definite species. According to Hayden, it is found in thin layers (from 5 to 20 cm. in thickness) in a metamorphic chalk-rock, on the Upper Missouri. On account of its softness it is cut into pipes by the Sioux Indians. These sections examined under the microscope show that it consists of a granular, colourless ground-mass which exerts but little action on polarised light, and of numerous crystals of a red mineral and quartz. The red crystals vary from 0·02 to 0·1 mm. in length (the commonest length being 0·04 mm.), and 0·02 to 0·03 mm. in width. They occur either spindle-like or in long ill-defined rhombic sections, whilst penetration-twins, somewhat resembling those of the staurolite according to the second law, are common. Owing to the crystals not being sufficiently transparent, their optical properties could not be determined, therefore the system in which they crystallise cannot be ascertained. Hydrochloric acid does not act on the mineral, the red colour remaining unchanged, even after prolonged boiling in the acid, from which the author concludes that the red crystals are those of a ferruginous zeolitic silicate, to which alone the name catlinite should be assigned. Jackson found the rock-mass contained from 5 to 7 per cent. of ferric oxide, and from 4·5 to 8·5 per cent. of water. C. A. B.

The Red Gneiss of the Saxon Erzgebirge. By H. Credner (*Jahrb. f. Min.*, 1878, 413—414).—The author's conclusions are as follows: viz:—

(1.) The red gneiss occurs in floe-like, lenticular interpolations and

more or less thick strata between the grey gneisses, micaceous gneisses, and gnessoid-mica-slates of the Erzgebirge and Saxon Mittelgebirge.

(2.) The red gneiss is intimately connected with the neighbouring archaic strata by a regular alternation of strata, or by a gradual passage over into the same.

(3.) The red gneiss exhibits a structural formation, which coincides in every respect with that of the archaic strata constituting its upper and lower walls.

(4.) The red gneiss is a normal member of the archaic series of strata of the above-mentioned districts, and a *sedimentary rock*. Red gneiss is consequently not an eruptive rock, as hitherto has been stated by other authors. C. A. B.

Serpentine from Verrayes (Aosta). By A. Cossa (*Bull. Soc. Chim.* [2], **31**, 130—131).—The serpentine of Verrayes is green, and contains grey metallic-looking lumps of magnetite; it breaks easily with a scaly fracture and irregular surface. Deprived of its magnetite mechanically, its mean sp. gr. is 2·564. Thin prismatic crystals are disseminated throughout the magnetite, which resist the action of hydrochloric acid, but melt before the blowpipe. They were found to contain silica, magnesia, a very little lime, and chromic oxide; they are similar in composition to enstatite.

The serpentine melts with difficulty, then blackens, and finally becomes decolorised in the oxidising flame. It gives off water in a closed tube, and does not contain a trace of carbonaceous matter. Hydrochloric acid decomposes it, yielding a gelatinous silica. Its composition is—

SiO_2.	P_2O_5.	MgO.	Fe_2O_3.	Cr_2O_3.	NiO.	CaO.	H_2O.
40·86	trace	41·37	4·59	0·03	0·09	0·03	13·08 = 100·05.

J. W.

Some Syenite-Porphyries of South-west Norway. By T. Liebisch (*Jahrb. f. Min.*, 1878, 412—413).—In a specimen from the Hofe Ris, the felspar was found to be oligoclase containing numerous interpolations and enclosures. The interpolated substance was a mono-symmetrical felspar, enclosing numerous plagioclases with a very fine twin-striation, also augite, biotite, olivine, magnetite, &c. The fine-grained ground-mass consisted of a mixture of orthoclase, plagioclase, augite, apatite, biotite, magnetite, and olivine, the latter being recognisable by the naked eye. The syenite-porphyry vein of Vettakollen contains tabular plagioclase suspended in a black, dense ground-mass, the latter consisting of a mixture of plagioclase, biotite, a light-green mineral which is probably augite, and some apatite and magnetite. The author does not consider the Vettakollen rock to be a true syenite-porphyry, on account of the absence of orthoclase. Specimens of the syenite-porphyry penetrating the Silurian formation of Sundvolden in Ringeriget, microscopically examined, were found to consist of a crystalline fine-grained ground-mass, with predominating orthoclase and some plagioclase, also numerous biotite crystals and augite in parallel growth with hornblende. The augite crystals were often surrounded by dark-green hornblende. C. A. B.

An Intergrowth of two Micas from Middletown, Connecticut. By A. v. Lasaulx (*Jahrb. f. Min.*, 1878, 630).—In a specimen examined by the author, it was observed that on one portion a light-coloured mica surrounded a dark-coloured mica, but the latter eventually spread out irregularly, penetrating and occasionally surrounding small particles of the light-coloured mica. A very careful determination of the optical properties of the two varieties (given at some length in the author's paper) proved that they were actually twinned, the twin plane being a face of ∞P, and the planes of symmetry of the two individuals intersecting under an angle of 60°; this twin formation being completely analogous to that often observed in the case of the phlogopite of Burgess. The light-coloured mica was muscovite, whilst the dark-coloured mica was a biotite resembling meroxene or the lepidomelane of Tschermak, having the following composition, viz.:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	K_2O.	Na_2O.
35·61	20·03	0·13	21·85	1·19	5·23	9·69	0·52

LiO.	TiO_2.	Fl.	Cl.	H_2O.
0·93	1·46	0·76	trace	1·87 = 99·27.

A peculiar decomposition was observed to have taken place upon the outer edge of the dark-coloured mica, resulting in the formation of a semi-translucent grey-green zone. This secondary formation exhibited the properties of true lepidomelane, the ferrous oxide of the original brown mica having been oxidised to ferric oxide, and deposited in cracks on the cleavage planes of the mineral. The author observed that the angle of the optical axes decreases as the brown colour increases, thus confirming Tschermak's conclusion that the angle of the optical axes increases with the amount of iron present in the mica, *combined* and not separated out. The above-mentioned intergrowth is remarkable (1) owing to the micas being optically dissimilar, and (2), as a further proof of the influence exerted by the chemical composition upon the dimensions of the angle of the optical axes. C. A. B.

Twin Zircon Crystals. By O. Meyer (*Jahrb. f. Min.*, 1878, 410—411).—Zircon occurs very commonly in microscopical crystals in the hornblende-slate and mica-slate of St. Gotthard, exhibiting the combination ∞P.P; twins being common according to the law, "the twin plane a face of P∞." The crystals are either nutmeg-brown or grey in colour, sometimes colourless, occasionally grouped together, and accompanied by iron-glance and iron-pyrites. Twin crystals of zircon have lately been found in the eklogite of the Bacher Gebirger in Styria, by Hussak. C. A. B.

New Mineral Occurrences in the Iron-ore District of Moravicza, in the Banat. By V. von Zepharowich (*Jahrb. f. Min.*, 1878, 409).—*Magnetic Pseudomorph after Iron-glance.*—Small, well-developed hexagonal lamellæ arrange themselves longitudinally, rosette-like, or superimposed on each other into long, narrow, reed-like leaves, which intersect each other under various angles. The individual leaves are united with the others by lateral branches, so that the aggregate

appears to be penetrated by cleft-like hollows. Examined under the microscope the individuals exhibit either a triangular striation or a peculiar parallel arrangement of triangular plates upon the surface, the latter being in reality extremely small octohedrons. Some of the individuals are separated from each other by interpolations of red garnet, white calcite, grey quartz, and grammatite. All have a black streak and are magnetic.

Varieties of Pyroxene (*Augite*).—Drusy *fassaite* occurs in hollow spaces resting upon rhombic dodecahedrons of fine-grained magnetite. The fassaite crystals attain a height of 10 mm. and a breadth of 3 mm., and generally exhibit the following forms in combination, viz.: $\infty P\infty$. ∞P.—$2P.2P\infty$, all of them being more or less decomposed and often converted into a greenish-yellow or ochre-yellow mass. Their occurrence upon decomposed magnetite and garnet warrants the assumption that they contain alumina and ferric oxide, like the fassaite of South Tyrol, which occurs also in the contact-zone between limestone and eruptive rocks.

Bismuthine is found disseminated in small granular particles (occasionally having a short columnar structure) in grammatite, sometimes being interposed between the fibres of that mineral.

Grammatite is found disseminated in white radio-fibrous masses, which are sometimes changed into a soft steatitic substance.

Ludwigite is found in finely fibrous or thin columnar masses.

C. A. B.

Mineralogical Notes. By A. E. Nordenskiöld (*Jahrb. f. Min.*, 1878, 406—407).—*Clevite.*—A new mineral from Garta, near Arendal. It is related to uranium-pitchblende, and resembles the latter in its external appearance. It was found to have the following chemical composition, viz.:—

U_2O_3.	UO.	PbO.	Fe_2O_3.	Y_2O_3,Er_2O_3.	Ce_2O_3.	ThO_2.
40·60	23·07	10·92	1·02	9·99	2·25	4·60

CaO.	MgO.	$H_2O.CO_2$.	Insoluble residue.
0·86	0·14	4·96	2·34 = 100·75.

The UO was determined by titration with potassium permanganate solution. The ratio of the erbia to the yttria was found to be as 33·52 : 66·48. Deducting the calcium and magnesium (expressed as carbonates), and assuming that 3 equivalents of ThO_2 replace 2 equivalents of sesquioxides, the author obtains the following formula for clevite, viz.: $(UOPbO)(U_2O_3Fe_2O_3Y_2O_3Er_2O_3Ce_2O_3ThO_2) + H_2O$. From this it would appear that clevite is a member of the spinelle group, containing, however, some water. On treating it with hydrochloric acid, lead chloride separates out, and a green solution is obtained which turns yellow on addition of nitric acid. It is infusible before the blowpipe, evolves water on being heated in the matrass, colours the microcosmic bead a deep green, which changes to yellow in the oxidising flame, and furnishes a lead bead on reduction with sodium carbonate on charcoal. Streak, blackish-brown, opaque, iron-

black, dull or shimmering. H. = 5·5; sp. gr. = 7·49. Crystals are rare, the forms observed being $\infty O\infty$.O. ∞O; occurs generally in grains in a dirty-brown felspar which is penetrated by cracks and rifts containing uranium-ochre. Clevite is accompanied by orthite, fergusonite, thorite, calcite, uranium-ochre, and *yttrogummite*. The last-named mineral is the final product of the decomposition of clevite, and is so named by the author. It has a resinous lustre, black or yellow colour (resembling orangeite), is translucent, contains water, yttria, and uranic oxide, has a conchoidal fracture, is homogeneous and isotropic. H. = 5. From the above properties it differs materially from the *gummite* derived from uranium-pitchblende. C. A. B.

Iodobromite, a New Silver-haloid. By A. v. Lasaulx (*Jahrb. f. Min.* 1878, 619—623).—This mineral was found by the author at the mine "Schöne Aussicht," in the district of Ems, Nassau, occurring in small, yellow, regular octohedrons accompanied by crystals of beaudantite. The vein-rock of this mine consists mostly of a ferruginous quartz, and the crystals of iodobromite are found in the numerous hollows in this vein-rock. They never exceed 3 mm. in size, but are very sharply defined; measurements with the telescope-reflecting goniometer being easily made and the interfacial angles found to be 109° 28′. The larger individuals do not exhibit such a brilliancy of lustre as the smaller ones, owing to their being built up of extremely small sub-individuals in a parallel position, their edges being also indented from the same reason. Sometimes two octohedral faces are abnormally developed, resulting in a tabular form. The "middle crystal" ($\infty O\infty$.O) was also a common combination, but a trapezohedron of undeterminable value was observed on only one crystal. The octohedral faces do not possess such a brilliant lustre as the cubical faces. Cleavage indistinctly octohedral. Colour mostly sulphur-yellow, although some are olive-green. These crystals are very malleable and can be pressed flat with the blade of a knife, which is characteristic of the silver haloïd-group. Heated in a matrass with hydrogen potassium sulphate, the bead is intensely red whilst hot, and orange or sulphur-yellow in the cold. A silver bead is obtained on heating the mineral on charcoal before the blowpipe, and bromine vapour is evolved. Iodine is also easily detected by the usual tests. The analysis of the mineral was carried out in the following way, viz.: a portion of the mineral was digested with dilute sulphuric acid and pure zinc, the silver which thus separated out was weighed and tested for purity; a few drops of a solution of nitrous acid in sulphuric acid were added to the solution containing chlorine, bromine, and iodine, and the mixture repeatedly shaken up with bisulphide of carbon until the latter was no longer coloured. The amount of iodine dissolved in the bisulphide of carbon was determined by titration with sodium thiosulphite. The chlorine and bromine were precipitated together by silver nitrate and the precipitate weighed; then a portion of the precipitate was heated in a stream of chlorine, and from the loss in weight of the residue the amount of silver bromide present was calculated. The result of the analysis was as follows, viz.:

	Ag.	I.	Br.	Cl.	
Found	59·96	15·05	17·30	7·09 =	99·40
Calculated ..	60·88	14·15	17·18	7·79 =	100·00

the formula corresponding with the above analysis being 2Ag(ClBr) + AgI. Specific gravity at 18° C. = 5·713. Iodobromite is the first instance of the three haloïds occurring crystallised together in nature. C. A. B.

The Rock of the St. Gotthard-Tunnel. By O. Meyer (*Jahrb. f. Min.*, 1878, 413).—The quartz of the southern slates of St. Gotthard contains a very large number of enclosures of liquid carbonic acid. The quartz of the granite-gneiss and gneiss of the northern portion of the tunnel does not contain any such enclosures. There are enclosures of liquid carbonic acid in the calcite of the calcium-mica slates, an occurrence which has never before been observed in calcite. The slates of this district enclose large quantities of specular-iron, staurolite, tourmaline, and zircon. The hornblendic slates of the southern portion of the tunnel contain numerous calcite crystals. The chlorite-like mineral which is found 797 mm. from the northern entrance, is helminth, which crystallises either rhombic or monosymmetrical, but not hexagonal. C. A. B.

The Meteoric Iron of Hungen. By Buchner and Tschermak (*Jahrb. f. Min.*, 1878, 411—412).—This meteorite fell on the 17th of May, 1877, at Hungen, in Upper Hesse. Fractured surfaces exhibit a grey ground-mass of a chondrodite character, with numerous enclosures of iron and troilite. A microscopical examination showed that about half of the outer crust consisted of iron, whilst the ground-mass was transparent and colourless. A portion of the same meteorite in the Vienna collection resembles closely the Pultusk meteorite according to Tschermak, only the outer crust is somewhat thicker on the Hungen meteorite. A section examined under the microscope showed the presence of particles of iron 1·5 mm. in size, and grains of magnetic iron-pyrites suspended in a mass consisting of globules. There were also present many non-transparent bodies, which were in all probability chromite or picotite. The transparent minerals (according to Tschermak) are olivine, bronzite, and diallagite. C. A. B.

Alkaline Constituent of the Hunyadi János Springs at Buda-Pest. By R. Fresenius (*Zeitschr. Anal. Chem.*, 1878, 461—465).—This water has been frequently analysed by different chemists, and the author gives the results of a recent analysis made by himself. The essential difference between his results and those formerly published is the entry of magnesium bicarbonate as the alkaline constituent, instead of sodium or calcium bicarbonates, as has been formerly done. The following experiments have induced the author to make this alteration. Turmeric paper was dipped into a very dilute solution of sodium bicarbonate (1), into a solution of magnesium bicarbonate (2), into a solution of calcium bicarbonate (3), and into Hunyadi János water (4). No alteration of colour is produced until the papers are hung in the air, when all of them become brown, that moistened with the sodium bicarbonate solution rather darker than the rest. If

the papers are allowed to become quite dry in the air, strip (1) appears very dark brown, strips (2) and (4) scarcely brown, and (3) somewhat lighter than (2) and (4). Hence it appears that the Hunyadi János water contains no sodium bicarbonate.

The following solutions were then heated to boiling and kept boiling for some time: calcium bicarbonate in carbonic acid (1), magnesium bicarbonate in carbonic acid (2), solution (2) which has magnesium sulphate dissolved in it (3), and Hunyadi János water (4).

Solution (1) soon became turbid, the calcium carbonate separated out almost completely, and the liquid did not alter the colour of the turmeric paper. Solution (2) soon became turbid, the magnesium being separated, but not completely; the liquid coloured turmeric paper brown, the colour disappearing almost completely on drying. Solution (3) did not become turbid on boiling; basic magnesium carbonate separated only after boiling for 10—20 minutes; the liquid coloured turmeric paper brown, but the colour disappeared almost completely on drying the paper in the air. Hunyadi János water (4) behaved precisely like (3), the filtrate containing all the lime as calcium sulphate. The substance which in (3) and (4) coloured turmeric brown, the colour disappearing when the paper is dried, is magnesium carbonate dissolved in a solution of magnesium sulphate. Sodium carbonate cannot be present in (4), since the reaction with turmeric paper is not given, and also because sodium carbonate could not coexist with calcium sulphate. Both sets of experiments prove that the alkaline substance in Hunyadi János water is not sodium carbonate or bicarbonate; that it is not calcium carbonate is proved by the fact that no calcium carbonate separates on boiling; there remains therefore only magnesium carbonate, and the evidence of all the reactions tends to prove that the alkalinity is caused by magnesium carbonate.

The author's analysis of the Hunyadi János water gives the following results:—

	Carbonates reckoned as monocarbonates, and all the salts estimated as anhydrous.	Carbonates reckoned as bicarbonates, and all the salts estimated as anhydrous.
Sodium sulphate	19·662123 p.m.	19·662123 p.m.
Magnesium sulphate	18·489451 „	18·449451 „
Calcium sulphate	1·321938 „	1·321938 „
Potassium sulphate	0·132943 „	0·132943 „
Sodium chloride	1·424068 „	1·424068 „
Magnesium carbonate	0·731347 „	1·114434 „
Ferrous carbonate	0·002059 „	0·002840 „
Silicon	0·011218 „	0·011218 „
Total	41·735147 „	42·119015 „
CO_2 half-combined	0·383868 „	—
CO_2 free	0·012683 „	0·012683 „
Sum of all the constituents	42·131698 „	42·131698 „

The following substances are also present, but in quantities too small to be estimated; lithia, strontia, phosphoric acid, nitric acid, boric acid, bromine, iodine, organic matter, and nitrogen gas. A litre of the water at 10·6° C. contains 6·955 c.c. free CO_2, and 217·44 c.c. free and half-combined. F. C.

Organic Chemistry.

Halogen Derivatives of Ethane. By W. Städel (*Liebig's Annalen*, **195**, 180—205).—The chlorobromo substitution-products of ethane and the results of the author's experiments on the action of chlorine on ethyl chloride, ethylidene chloride, ethylene chloride, dichlorethyl chloride, and monochlorethyl chloride have been previously described (this Journal, 1879, 212) and (*Ber.*, **10** and **11**). The following are the most important results. (1.) By the action of chlorine on ethyl chloride, only $CH_3.CHCl_2$ is formed in the first instance, whilst ethylidene chloride yields $CH_3.CCl_3$ and $CH_2Cl.CHCl_2$. (2.) Ethyl chloride on bromination yields $CH_3.CHBrCl$. α-Chlorobromethane gives $CH_3.CBr_2Cl$ and $CH_2Br.CHBrCl$. On brominating ethylidene chloride and ethyl bromide, only $CH_3.CBrCl_2$ and $CH_3.CHBr_2$ are formed. These experiments show that the halogen elements replace by preference those hydrogen atoms which are combined with an atom of carbon to which a halogen atom is already attached. W. C. W.

Nomenclature and Boiling Points of the Chlorobromo Substitution-products of Ethane and Ethylene. By J. Denzel (*Liebig's Annalen*, **195**, 210—218).—The author proposes to distinguish the isomeric halogen substitution-products of ethane and ethylene by the following system of nomenclature.

When 3 isomerides exist, the halogen atoms are as far as possible attached to the same carbon atom in the α-modification, whilst in β the halogen possessing the strongest affinity is isolated from the other halogens, *e.g.*, chlorodibromethane α, $CH_3.CBr_2Cl$; β, $CH_2Br.CHBrCl$; γ, $CHBr_2.CH_2Cl$; dichlorobromethane α, $CH_3.CBrCl_2$; β, $CH_2Br.CHCl_2$; γ, $CHBrCl.CH_2Cl$.

When 4 isomerides are possible in β, the most powerful halogen and the next most powerful are attached to the same carbon atom, whilst in γ the most powerful and third strongest halogen are attached to the same carbon atom, and in δ, the most powerful halogen atom is, as far as is possible, separated from the other halogens, *e.g.*, chlorobromiodethane α, $CH_3.CIBr.Cl$; β, $CH_2I.CHBrCl$; γ, $CH_2Br.CHICl$; δ, $CHBrI.CH_2Cl$; trichlorobromiodethane α, $CHIBr.CCl_3$; β, $CHICl.CBrCl_2$; γ, $CHBrCl.CICl_2$; δ, $CIBrCl.CHCl_2$.

The tabular statement of the boiling points of the chlorobromo substitution-products of ethane and ethylene contained in this paper, shows that the boiling point of a compound is raised about 25° by the replacement of chlorine by an atom of bromine, *e.g.*, chlorethane, b. p. 12°; bromethane, b. p. 39°; α-chlorobromethane, b. p. 85°; α-dibrom-

ethane, b. p. 110°; β-chlorobromethane, b. p. 105°; β-dibromethane, b. p. 130°. These numbers also show that the β-modification boils either 20° or 40° higher than the α.

The addition of a bromine atom to a chlorobromo substitution-product of ethane raises the boiling point about 40°, provided that the bromine combines with a carbon atom to which a halogen atom is already attached, if this is not the case the boiling point is raised 80°, *e.g.*:—

	B. p.	Difference.
$H_3C.CH_2Cl$	12°	—
$H_3C.CHBrCl$	85	73°
$H_3C.CBr_2Cl$.....	124	39
$H_2BrC.CBr_2Cl$.....	201	77
$HBr_2C.CBr_2Cl$.....	240	39

The first member of this series forms an exception to this rule.

The addition of an atom of bromine to the chlorobromethylenes raises the boiling point 80°. W. C. W.

Ethylidene Chlorobromide. By Reboul (*Bull. Soc. Chim.* [2], **30**, 497).—Lescœur's aldehyde chlorobromide is identical with the ethylidene chlorobromide discovered by the author (*Bull. Soc. Chim.*, **14**, 230). W. C. W.

Dextrogyrate Amyl Alcohol. By J. A. Le Bel (*Bull. Soc. Chim.* [2], **31**, 104).—Lævogyrate amyl alcohol can be rendered inactive by converting it into sodium amylate and heating the latter to a comparatively high temperature. In like manner the inactive alcohol can be rendered dextrogyrate by allowing certain fungoïd growths to propagate in it for a time. Thus a solution containing 3 grams of inactive alcohol, 1·25 grams of various salts, and a little yeast slightly acidulated, was impregnated with fungus or mould spores. At the end of a month the green vegetable growth having decayed, the liquid was distilled, and an alcohol isolated marking + 1·7° for a column 10 cm. in length.

The addition of a little dilute sulphuric acid when the mould begins to die off regenerates the vegetation in a remarkable manner. Among the fungi were distinguished the *mycoderma aceti*, and species of *oïdium* and *penicillium*, the latter existing in, if not preferring neutral solutions. In an experiment on a larger scale with a sample containing a small quantity of lævogyrate alcohol, −8°, the alcohol, after the action of the mould, has acquired a dextrorotatory power of + 28°, or altogether an increase of + 36°. When converted into amyl iodide, the latter was lævorotatory, −48° for 10 cm.; whereas it is well known that amyl iodide made from ordinary amyl alcohol is dextrorotatory. J. W.

Inversion of Cane-sugar, and Consecutive Alteration of the Glucoses so formed. By Durin (*Compt. rend.*, **87**, 754—755).—The author's experiments lead him to consider that the conversion of sucrose into glucose in the operations of sugar refining is not due to

the action of a ferment, nor to precontained glucose, but is of a purely chemical nature, and can be avoided. Solutions of pure sugar with a faintly alkaline reaction, containing 2, 3, 8, and 60 per cent. of glucose, undergo no change when heated at 70—75° for 36 to 40 hours, but on continuing the heating beyond this point from 85 to 114 hours, the alkalinity disappears, the solution becomes slightly acid, and inversion of the sugar begins, which, however, bears no relation to the proportion of pre-existing glucose. If the heating be still further prolonged, a general inversion results, which in mixtures of sucrose and glucose is not proportional to the quantity of sucrose present; if the alkalinity of the syrup be restored, no further inversion takes place.

Solutions of pure glucose are modified by prolonged heating, their rotatory power becomes lessened, the facility with which they undergo alcoholic fermentation diminishes, and the fermentation is often incomplete. Altogether there appears to be little necessity to imagine with M. Gayon the intervention of a ferment as essential to inversion, more especially as the inversion is proportional to the temperature at which the operation proceeds, which could not happen if the action were a purely fermentative one. There can be little doubt but that the phenomenon is essentially *chemical* in its nature as opposed to *fermentative*, and that although we cannot determine its equation, we can observe that it acquires its maximum activity when the solutions are neutral or acid, and that it is suspended altogether when the liquids are alkaline. J. W.

Action of Diastase, Saliva, and Pancreatic Juice on Starch and Glycogen. By F. Musculus and J. De Mering (*Bull. Soc. Chim.* [2], **31**, 105—116).—That the body produced by the action of diastase on starch is maltose and not dextrose has been placed beyond doubt by the experiments of Dubrunfaut, O'Sullivan, and Schultze. They have examined its optical and reducing properties, have prepared it in a pure state, and generally have established its chemical relations in such a manner as to render it easy to be recognised when met with under varying circumstances. The action of saliva on starch, however, up to the present time was less accurately known. Nasse, in a paper published in *Pflüger's Archiv.*, Bd. **14**, showed that dextrose was not produced, but he endeavoured to prove that the substance formed was not maltose, but a new body which he termed *ptyalose*, basing his opinion upon the observation that the rotatory power of the so-called ptyalose, when boiled with dilute acids, instead of increasing by one-third, became twice as great as before treatment. The author's experiments upon this subject, which appear to have been conducted with great care, and are detailed in the original memoir at considerable length, show conclusively that the ptyalose of Nasse does not exist; that the principal product of the action of saliva on starch is maltose, together with certain reducing but non-fermentable dextrins, and a very small quantity of dextrose. They think that since Nasse did not obtain crystals—whilst they have isolated the sugar in a definite form, and compared its optical properties with those of maltose prepared from other sources—the substance which he

operated on was most probably a mixture of maltose and dextrin, which would easily account for the reducing or rotatory power being doubled on boiling with acids, instead of being increased by one-third, more especially as they have themselves shown that under similar circumstances the reducing power of these dextrins is often increased to three or four times its original value.

The authors offer some very pertinent remarks respecting the reducing power of dextrin. Various opinions have been held with regard to this property, of which perhaps the one most generally received is that it is not a quality of dextrin at all, but is referable entirely to the sugar with which the dextrin is contaminated. They point out that a non-reducing dextrin has never been obtained, either by continued washing with alcohol or by repeated fermentations; that the method adopted by Brücke and Bondonneau for purifying the dextrin by boiling it for half an hour with a solution of copper oxide in caustic potash, whereby they obtained a non-reducing residue, does not prove that the reducing power was due to sugar, and moreover is open to objection, since in the operation, the greater part of the dextrin is destroyed, so that it becomes quite possible to conceive that the molecular structure of the residue has been also modified, which would be sufficient to account for its altered action. Even such modification is but ephemeral, for Bondonneau states that the reducing power reappears after a few minutes' contact with water, which he proceeds to explain by supposing that a small quantity of dextrose has been suddenly formed under the influence of certain non-coagulable albuminoïd substances, which having escaped destruction act as a ferment, hydrating the dextrin as soon as it has been dissolved. This latter hypothesis appears to the authors to accord little with the known properties of diastatic ferments, which will not resist the action of boiling water, and would be therefore still less likely to withstand the action of boiling potash.

The action of the pancreatic fluid on starch is shown to be identical with that of saliva, transforming the starch into maltose, dextrin, and dextrose.

Glycogen submitted to the action of saliva or diastase is likewise resolved into dextrin and maltose, saliva converting it more easily than diastase. The dextrins of glycogen, however, differ from those of starch, in that they are less hygroscopic, and possess an inferior reducing power. In addition to this, the dextrin obtained from starch by stopping the saccharification when the reducing power is 37° is still easily attacked by saliva and by diastase, whilst the dextrin from glycogen obtained when the reducing power of the liquor is likewise 37° is no longer attackable by these ferments. Glycogen obtained from the liver of animals fed on a nitrogenous and on a non-nitrogenous diet, or from animals of different genera, behaved in a precisely similar manner with ferments, from which it is fair to conclude, at least as far as these experiments show, that only one variety of glycogen exists. J. W.

Nitro-derivatives of Cellulose. By G. Wolfram (*Dingl. polyt. J.*, **230**, 148—159).—In the second part of this paper (for first paper

see this vol., 218), the author continues his researches on cellulose. The results obtained in this and the former paper may be condensed in the following:—

1. By the action of nitrosulphuric acid on cellulose, nitro-compounds are obtained, the composition and properties of which vary in accordance with the quantity of nitric and sulphuric acids, the quality of cellulose, the time the reaction continues, and the temperature of the acid mixture.

2. Four nitro-compounds of cellulose exist:—

Pentanitrocellulose, $C_{12}H_5(NO_2)_5O_{10}$
Tetranitrocellulose, $C_{12}H_6(NO_2)_4O_{10}$
Trinitrocellulose, $C_{12}H_7(NO_2)_3O_{10}$
Dinitrocellulose, $C_{12}H_8(NO_2)_2O_{10}$.

3. These compounds may be obtained in a fibrous or pulverised state.

4. The amount of NO_2 present in the nitro-compounds increases with the quantity of sulphuric acid, the concentration of the nitric acid, the time of action, and the temperature.

5. By increasing the temperature of the acid mixture, the quantity NO_2 is not merely increased, but the penetration of the cellulose facilitated and the structure of the latter altered, yielding a pyroxylin of different physical properties.

6. The products obtained by nitrating cellulose are mostly mixtures of various stages of nitration, which with exception of pentanitrocellulose are prepared only with difficulty, and cannot be separated by solvents except in a very imperfect manner.

7. Nitro-compounds of cellulose with more than 41·89 per cent. of NO_2 contain nitric acid in the pores, which is not removable by washing; those containing less than 22·22 per cent. of NO_2 are mixed with non-nitrated cellulose.

8. The various kinds of cellulose are converted into the same compound by concentrated sulphuric and nitric acids; weaker acids, however, yield compounds of different degrees of nitration.

9. The more easily a fibre is toughened by the action of sulphuric acid, the more difficult it will be to convert it into nitrated compounds.

10. Toughened pyroxylins are distinguished from untoughened by being partially reduced when treated with a boiling solution of ferrous sulphate, and by becoming coloured with iodine solution.

11. The solubility of nitro-cellulose varies with the composition and the structure.

12. The formation of a vitreous layer by evaporating a solution of pyroxylin is not merely dependent on the substance, but also on the solvent used.

13. By impregnating cotton with gelatin, or by adding gelatin to the acid mixture previous to nitration, a partly pulverised pyroxylin may be obtained. D. B.

Diallylacetic Acid. By Reboul (*Bull. Soc. Chim.* [2], **30**, 498).—The author claims priority to the discovery of diallylacetic acid. W. C. W.

Fumaric and Maleic Acids. By C. Petri (*Liebig's Annalen*,

195, 56—78).—Kekulé's observation, that whilst fumaric acid on treatment with bromine and water yields dibromosuccinic acid, maleic acid under similar conditions gives a mixture of dibromo- and isodibromosuccinic acids, is explained by the fact that the bromine first converts a portion of the maleic acid into fumaric acid, which is afterwards changed into dibromosuccinic acid. By boiling with water dibromosuccinic acid is decomposed into hydrobromic acid and bromomaleic acid (m. p. 128°). A mixture of fumaric and succinic acids is obtained by the action of sodium amalgam on bromomaleic or on isobromomaleic acid. Maleic and fumaric acids yield maleic anhydride on distillation; similarly monobromo- and isobromo-maleic acids form monobromomaleic anhydride on distillation. By the action of hydrobromic acid, bromomaleic acid is converted partly into isobromomaleic and partly into dibromosuccinic acids.

From these experiments the author concludes that there is but one bromomaleic acid, that the so-called isobromomaleic is in reality bromofumaric acid, and that Kekulé's meta- and para-bromomaleic acids consist of impure bromomaleic and bromofumaric acids. The existence of these acids is, according to the author, the only fact which cannot be explained by his constitutional formulæ for fumaric and maleic acids (*Annalen*, **188**, 95).

Tribromosuccinic acid, prepared by the action of bromine and water on bromomaleic or bromofumaric acids, forms small transparent deliquescent needle-shaped crystals (m. p. 136°), which are soluble in water, alcohol, ether, and in benzene. *Dibromacrylic acid*, $C_3H_2BrO_2$, prepared by boiling the preceding compound with water, crystallises in glistening plates, soluble in alcohol, ether, and in hot water. It melts at 85°, and boils at 243—250°. The ethyl salt is a colourless liquid, boiling at 212°. Bourgoin's tribromosuccinic acid (*Compt. rend.*, **78**, 1141) appears to be a mixture of dibromofumaric and dibromosuccinic acids. W. C. W.

Some New Platinum-compounds: Fulminoplatinums. By E. v. Meyer (*J. pr. Chem.* [2], **18**, 305—324).—Fulminoplatinums (Knallplatine) is the name given by the author to a number of bodies obtained by the action of potash on ammonium chloroplatinate, $PtCl_4(NH_4Cl)_2$. These bodies are nearly insoluble in water, and do not form definite compounds with either acids or alkalis. The nitrogen contained in them is so firmly held in combination that they give off no ammonia when boiled with strong potash solution. When heated *per se* they undergo total decomposition, generally with explosive violence, owing to the sudden liberation of a large quantity of nitrogen.

When ammonium chloroplatinate is boiled with a quantity of aqueous potash insufficient for complete decomposition, added very slowly, a product of the formula $PtNClO_3H_6$ is obtained, the formation of which may be represented thus:—

$$PtCl_4(NH_4Cl)_2 + 5KOH = 5KCl + 2H_2O + NH_3 + PtNClO_3H_6.$$

The chemical behaviour of this body, and the existence of other bodies standing in simple relations to it, show, however, that the fore-

going formula must be quadrupled, making it $Pt_4N_4Cl_4O_{12}H_{24}$ (*tetrachlorofulminoplatinum*). Its relations to the other fulminoplatinums may then be exhibited by the following equations, which indicate the derivation from it of (1) *trichloroxyfulminoplatinum*, (2) *dichlorofulminoplatinum*, and (3) *chloroxyfulminoplatinum*:—

(1.) $Pt_4N_4Cl_4O_{12}H_{24} + KOH = KCl + Pt_4N_4Cl_3(OH)O_{12}H_{24}$.
(2.) $Pt_4N_4Cl_4O_{12}H_{24} + 2KOH = 2KCl + Pt_4N_4Cl_2O_{12}H_{22} + 2H_2O$.
(3.) $Pt_4N_4Cl_4O_{12}H_{24} + 3KOH = 3KCl + Pt_4N_4Cl(OH)O_{12}H_{22} + 2H_2O$.

The constitution of these bodies is as yet undetermined.

Tetrachlorofulminoplatinum, $Pt_4N_4Cl_4O_{12}H_{24}$, is obtained only with great difficulty, one of its atoms of chlorine being very easily eliminated. It is formed on heating ammonium chloroplatinate with aqueous potash (4·6 mols.), added very slowly until a temporary alkaline reaction is produced. The pale yellow precipitate is purified by repeated boiling with very dilute acetic acid and water. A slight excess of potash determines the formation of bodies containing less chlorine.

Tetrachlorofulminoplatinum when digested with aqueous ammonia gives up half its chlorine, and when evaporated with ammonia over the water-bath, it loses three-fourths of its chlorine; whence it appears that two atoms of chlorine are eliminated easily, and a third with more difficulty, whilst the fourth is firmly held in combination. The bodies formed by the action of ammonia explode violently when heated; they have not been fully investigated. When gently heated with oxalic acid in presence of dilute sulphuric acid, tetrachlorofulminoplatinum gives off a quantity of carbonic anhydride corresponding to a loss of 3 atoms of oxygen from each mol. At 150° it gives off 4 mols. of water.

Trichlorofulminoplatinum, $Pt_4N_4Cl_3(OH)O_{12}H_{24}$, is formed when ammonium chloroplatinate is decomposed with an insufficient quantity of potash (4·5—5 mols.), added in small portions somewhat rapidly. At 150°, it loses 3 mols. of water, and when more strongly heated, it explodes, giving off gases which consist mainly of nitrogen but contain also free oxygen. When treated with ammonia, it gives up 2 atoms of chlorine. It is acted on by oxalic acid in the same manner as the previous compound, the carbonic anhydride evolved corresponding with a loss of 3 atoms of oxygen from each molecule. After the reaction the liquid contains a black precipitate, which gives off ammonia when heated with soda. When gently heated in hydrogen, the trichloro-compound undergoes violent decomposition, yielding water, ammonia, and free nitrogen.

Dichlorofulminoplatinum, $Pt_4N_4Cl_2O_{12}H_{22}$, is formed on heating ammonium chloroplatinate with aqueous potash, added in moderate quantities until the liquid remains slightly alkaline and ceases to evolve ammonia. It is a fine yellow body, closely resembling the compound last described in most of its reactions. It is completely decomposed by treatment with zinc and sulphuric acid, the platinum being thrown down in a finely divided metallic state, whilst the whole of the chlorine goes into solution. Sulphur dioxide passed into water in

which the compound is suspended, gradually dissolves it, forming a nearly colourless solution, which when neutralised with sodium carbonate and evaporated yields crystals of Birnbaum's salt,

$$(PtSO_3.3Na_2SO_3)_2.3H_2O$$

(*Annalen*, **139**, 169).

Chloroxyfulminoplatinum, $Pt_4N_4Cl(OH)O_{12}H_{22}$, is obtained as a dark yellow powder by heating ammonium chloroplatinate with 4·7 mols. of aqueous potash added at once, until ammonia is no longer evolved. It loses 4 mols. of water at 152°. When gradually heated to 260° with sodium carbonate, nearly the whole of the hydrogen is oxidised to water, whilst the nitrogen is for the most part set free. It is not appreciably acted on by oxalic acid. With nascent hydrogen, it behaves like the preceding compound.

The foregoing results show that the decomposition of ammonium chloroplatinate by potash results in the formation of bodies containing equal numbers of atoms of platinum and nitrogen, whence it follows that ammonium chloroplatinate cannot be regarded as a double salt of platinic chloride and ammonium chloride, $PtCl_4(NH_4Cl)_2$, the two atoms of nitrogen having essentially different functions in the compound. The author has found by direct experiment that when ammonium chloroplatinate is heated even with a large excess of potash, only half the nitrogen is eliminated in the form of ammonia. J. R.

Synthesis of Uric Acid Derivatives; Alloxan, Uramil, Murexide, &c. By E. Grimaux (*Compt. rend.*, **87**, 752—753).—By heating to 150° a mixture of malonic acid and urea with excess of phosphorus oxychloride, an amorphous yellow mass is obtained, from which, by further treatment, several uric acid derivatives can be prepared.

The crude product is dissolved in nitric acid, and hydrogen sulphide passed in until the solution gives a violet precipitate with baryta-water. After filtering off the sulphur and allowing the liquor to remain for 48 hours, a deposit of crystals is obtained which gives all the characteristic reactions of *alloxantin*. Thus, with baryta-water their solution gives a violet precipitate, which becomes white on boiling. Dissolved in nitric acid, they furnish a crystalline precipitate of *alloxan* on addition of potassium cyanide and ammonia; and the acid solution, when boiled with sal-ammoniac, becomes filled with slender, almost insoluble needles of *uramil*. This uramil, when heated with water and silver oxide yields a deep purple liquor, from which *murexide* crystallises with all its eminently characteristic properties. There can be no question, therefore, but that the substance originally obtained from malonic acid by synthesis was alloxantin. Such being the case, it enables us to realise the synthesis of the whole of the derivatives of uric acid, since allantoïn and the parabanic derivatives have been already prepared from other sources.

The reaction of urea and phosphorus oxychloride with malonic and tartronic acids may be used as a qualitative test for these substances. One centigram of the acid, with about the same quantity of urea, is heated with two or three drops of the oxychloride, and then treated successively with nitric acid and with ammonia. In this manner a rich

purple colour is developed identical with that furnished by uric acid under similar circumstances. J. W.

Hydrogenation of Benzene and Aromatic Compounds. By Berthelot (*Ann. Chem. Phys.* [3], **15**, 150—157). — The author described some ten years ago a method for saturating organic compounds with hydrogen; this method consisting in treating the substance with a large excess of a saturated solution of hydriodic acid at a temperature of from 270—280°. In this paper he shows the results obtained by applying this method to benzene and the aromatic series, and finds that a sufficiently intense and prolonged action of hydriodic acid transforms all such hydrocarbons to the state of saturation, such as hexylic hydride, $C_{12}H_{14}$, volatile at about 69°; this maximum of saturation being, according to the author, identical for the fatty and aromatic series. J. M. T.

Dinitrochlorobenzene. By Beilstein and Kourbatoff (*Bull. Soc. Chim.* [2], **30**, 537).—A chlorophenylene diamine (m. p. 86°) is formed by the reduction of dinitrochlorobenzene (m. p. 50°). W. C. W.

Formation of Unsaturated Hydrocarbons from the Addition-products of Non-saturated Acids. By R. Fittig (*Liebig's Annalen*, **195**, 169—179).—The addition-products of certain unsaturated acids with hydrobromic acid yield hydrocarbons, when treated with a solution of sodium carbonate. This only appears to be the case when the atom of bromine and the carboxyl group are both attached to the same carbon atom. The formation of hydrocarbons from hydrobromocumenyl-crotonic and analogous acids by Perkin (this Journal, 1877, 660) would be an exception to this rule, but the author considers that the constitution of these acids has not been satisfactorily proved by Perkin. W. C. W.

Compounds of Metallic Salts with Compound Ammonias. By A. Destrem (*Bull. Soc. Chim.* [2], **30**, 452).—A brown crystalline powder, having the composition $CuCl_2 2(C_6H_7N)$, separates out when phenylamine is added to an alcoholic solution of cupric chloride. The hydrochloride, $CuCl_2 2(C_6H_7N.HCl)$, is obtained in yellow tabular crystals, by mixing an alcoholic solution of cupric chloride with phenylamine hydrochloride, or by dissolving the preceding compound in hydrochloric acid. W. C. W.

Action of Aniline, Toluidine, and Naphthylamine on Cholesteryl Chloride. By Valitsky (*Bull. Soc. Chim.* [2], **30**, 535).—*Cholesterylaniline*, $C_{26}H_{43}.C_6H_5NH$, prepared by the action of aniline on cholesteryl chloride at 150°, crystallises in rectangular plates, which melt at 187°. It is soluble in carbon bisulphide. *Chloresteryltoluidine*, $C_{26}H_{43}.C_7H_7NH$, melts at 172°, and is soluble in carbon bisulphide. The *α-napthylamine* compound, $C_{26}H_{43}.C_{10}H_7NH$, melts at 202°, and is less soluble in carbon bisulphide than the preceding compounds. W. C. W.

Aniline Derivatives of Sebacic Acid. By E. Maillot (*Compt.*

rend., **87**, 737).—Equal weights of sebacic acid and aniline, heated to a temperature of 150°, produce:—

1. A neutral compound, soluble in boiling absolute alcohol; *sebanilide*.

2. An acid body, *sebanilic acid*, soluble in alcohol and ether, which is monobasic, and capable of forming salts. J. W.

Metaiodonitro- and Metaiodamido-benzoic Acids. By A. Grothe (*J. pr. Chem.* [2], **18**, 324—327).—The author has obtained three isomeric nitro-acids, and the corresponding amido-acids by the action of concentrated nitric acid on metaiodobenzoic acid. The isomeric nitro-acids were separated by fractional crystallisation of the barium salts.

α-Metaiodonitrobenzoic acid (m. p. 235°) is white, sparingly soluble in water, and still less in water containing hydrochloric acid; it dissolves easily, however, in solutions of the *β*- and *γ*-acids.

The *barium salt*, $[C_6H_3I(NO_2).COO]_2Ba + 3H_2O$, forms white glistening needles, which lose their water of crystallisation at a gentle heat. The *calcium salt*, $[C_6H_3I(NO_2).COO]_2Ca + 2H_2O$, forms long glistening yellow laminæ. The *strontium salt*, $[C_6H_3I(NO_2).COO]_2Sr + 4H_2O$, white shining needles. The *ammonium salt*, $C_6H_3INO_2.COONH_4 + H_2O$, indistinct needles. The *sodium salt*, $C_6H_3I(NO_2).COONa + 3H_2O$, indistinct needles. The *magnesium salt* forms hygroscopic laminæ. The zinc, lead, mercury, silver, and copper salts were also prepared.

Ethyl salt, $C_6H_3I(NO_2).COOC_2H_5$, obtained by heating the silver salt with ethyl iodide, melts at 84°.

β-metaiodonitrobenzoic acid (m. p. 174°) is of a yellowish-white colour. It is easily soluble in water, and more so in acidulated water; it melts in boiling water, forming a colourless oil. The *barium salt*, $[C_6H_3I(NO_2).COO]_2Ba + 6H_2O$, forms fine yellow sharp needles, efflorescent in the air.

The *calcium salt*, $[C_6H_3I(NO_2)COO]_2Ca$, crystallises in sharp white needles. The *ammonium salt*, $C_6H_3I(NO_2).COONH_4$, forms large yellow rectangular plates. The *strontium salt*, $[C_6H_3I(NO_2).COO]_2Sr$, reddish needles. The *potassium salt*, $C_6H_3I(NO_2).COOK + 3H_2O$, forms yellow hexagonal prisms. The *sodium salt*, $C_6H_3I(NO_2).COONa + 4H_2O$, crystallises in large yellow monoclinic plates. The *lithium salt*, $C_6H_3I(NO_2).COOLi + H_2O$, forms reddish needles.

The *ethyl salt* (m. p. 64°), $C_6H_3I(NO_2).COOC_2H_5$, forms large yellow plates, which are slightly soluble in alcohol, but easily soluble in ether.

γ-Metaiodonitrobenzoic acid (m. p. 192°) is of an intensely yellow colour. It is easily soluble in water, but does not melt in boiling water like the *β*-acid. The *barium salt*, $[C_6H_3I(NO_2).COO]_2Ba + 3H_2O$, crystallises in intensely yellow laminæ. The *calcium salt*, $[C_6H_3I(NO_2).COO]_2Ca + 3\frac{1}{2}H_2O$, crystallises in yellow laminæ; and the *strontium salt*, with $4H_2O$, crystallises in yellow needles. The *sodium salt*, $+ H_2O$, forms brilliant silky yellow needles.

α-Metaiodamiodbenzoic acid, $C_6H_3I(NH_2).COOH$ (m. p. 137°), forms fine dark-brown crystals, which are easily soluble in water.

$C_6H_3I(NH_2).COOH.HCl$ crystallises in reddish needles. *Barium salt* with 1 mol. of water forms rectangular plates, and the *strontium salt* forms indistinct crystals, which are hygroscopic. The *copper salt*, from which the free acid was isolated, forms brilliant green crystals, which are quite insoluble in water.

The action of nascent hydrogen on this acid produced an amidobenzoic acid (m. p. 143°), showing that the nitro and amido groups in the α-acids stands in the ortho position either as 1 : 2 or as 1 : 6.

β-Metaiodamidobenzoic acid (m. p. 209°), $C_6H_3I(NH_2).COOH$, is but sparingly soluble in water, crystallising therefrom in needles.

$[C_6H_3I(NH_2).COO]_2Ba$ crystallises in brilliant laminæ. The strontium and calcium salts form dark-coloured needles, the latter containing $2H_2O$.

Nascent hydrogen produces an amidobenzoic acid (m. p. 144°), showing also that in the β-acids the amido group stands in the ortho position. A. J. C.

Amidohydrocinnamic Acid (Phenylamidopropionic Acid). By E. Posen (*Liebig's Annalen*, **195**, 143—145).—When hydrobromocinnamic acid is gradually added to cold concentrated aqueous ammonia, a mixture of cinnamene and amidohydrocinnamic acid, together with a small quantity of cinnamic acid, is formed.

Amidohydrocinnamic acid, $C_6H_5.C_2H_3(NH_2).COOH$, is deposited on cooling its hot aqueous solution in colourless crystals (m. p. 121°), soluble in alcohol, but almost insoluble in ether and carbon bisulphide.

It does not combine readily with acids or with alkalis. On evaporation of an ammoniacal solution, crystals of the free acid are deposited, and the hydrochloric acid solution is decomposed by evaporation on the water-bath into ammonium chloride and cinnamic acid. W. C. W.

Addition-products of Cinnamic Acids. By R. Fittig and F. Binder (*Liebig's Annalen*, **195**, 131—143).—*Hydrobromocinnamic acid*, $C_9H_9BrO_2$, is formed by the action of cold fuming hydrobromic acid on cinnamic acid. After the crude product has been purified by recrystallisation from boiling carbon bisulphide, the acid is obtained in colourless scales, which melt at 137°, and begin to decompose at 143° into hydrobromic and cinnamic acids. *Hydriodocinnamic acid* forms colourless crystals, which melt at 119° with decomposition. These two acids are identical with Glaser's bromo- and iodo-derivatives of phenyllactic acid (*Annalen*, **147**, 96). Hydriodo- and hydrobromocinnamic acids are decomposed by a cold solution of sodium carbonate, forming cinnamene and small quantities of cinnamic and phenyllactic acids. The same products of decomposition are obtained on boiling the acids with water; 70 per cent. of the hydrobromocinnamic acid is converted into phenyllactic acid, but in the case of hydriodocinnamic acid, the chief product of the reaction is cinnamic acid.

Hydrodibromocinnamic acid, $C_9H_8Br_2O_2$, first prepared by Schmitt (*Annalen*, **127**, 319), is best obtained by adding a solution of bromine in carbon bisulphide, to a solution of cinnamic acid in the same sol-

vent. It is not decomposed by a cold solution of sodium carbonate, but splits up on boiling with water into β-bromocinnamene, phenylbromolactic acid, and a small quantity of cinnamic acid. A fourth substance, probably α-bromocinnamene, which decomposes on distillation, is also formed. W. C. W.

Atropic and Isatropic Acids. By R. Fittig and C. Wurster (*Liebig's Annalen*, **195**, 145—168).—*Atropic acid*, $C_6H_5.C(COOH)=CH_2$, is prepared by boiling atropine with baryta-water for several hours, and then decomposing the barium salt with hydrochloric acid. The pure acid is deposited in colourless glistening plates (m. p. 106·5°) from a solution of the crude product in a mixture of equal volumes of alcohol and water. The acid can be distilled under diminished pressure, and it is also volatile in a current of steam; but when subjected to a temperature between 100° and 140° for several hours, or boiled with water in a flask connected with an inverted condenser, it is converted into isatropic acid. This substance is insoluble in carbon bisulphide, ether, benzene, and petroleum-ether; it is sparingly soluble in boiling water, but dissolves more freely in alcohol and in glacial acetic acid. From a mixture of alcohol and water it is deposited in large opaque crystals, which melt at 240°.

Bromhydratropic acid, $C_6H_5.CH(CH_2Br).COOH$, is formed by treating atropic acid with cold fuming hydrobromic acid. The crystals obtained by recrystallising the crude product from low-boiling petroleum ether are dissolved in a small quantity of carbon bisulphide. On the addition of petroleum-ether to this solution, the pure acid separates out in transparent triclinic crystals (m. p. 93°), which are insoluble in water, but dissolve freely in other solvents. Bromhydratropic acid is decomposed by a hot solution of sodium carbonate, or by merely boiling with water, yielding *atrolactic* and atropic acid. When the decomposition is effected by sodium carbonate, only a small quantity of atropic acid is formed. Atrolactic acid, $C_9H_{10}O_3 + \frac{1}{2}H_2O$ [probably $C_6H_5.CH(CH_2.OH).COOH$], crystallises in transparent needles and plates, which lose their water of crystallisation at 85°. The anhydrous acid melts at 93—94°, and is freely soluble in water. These properties show that this substance bears some resemblance to Glaser's phenyllactic acid, but that it is quite distinct from tropic acid (m. p. 117°). Barium, calcium, and zinc atrolactates are crystalline salts, which are sparingly soluble in cold water.

On spontaneous evaporation of an ammoniacal solution of bromhydratropic acid, the corresponding amido-acid, $C_6H_5.CH(CH_2.NH_2).COOH$, is deposited in glistening scales (m. p. 169·5°), which are soluble in hot water. Small quantities of atropic and atrolactic acids are also formed at the same time.

Dibromhydratropic acid, $C_6H_5.CBr(CH_2Br).COOH$, prepared by adding bromine dissolved in carbon bisulphide to a solution of atropic acid in the same solvent, crystallises in silky needles, which dissolve in boiling carbon bisulphide, petroleum-ether, and chloroform. It melts at 115°, and decomposes at 140°. When treated with a solution of sodium carbonate, or boiled with water, it yields acetophenone: $C_9H_8Br_2O_2 + H_2O = C_8H_8O + H_2O + CO_2$. On heating it with

a small quantity of water in sealed tubes at 100°, monobromatropic acid, $C_9H_7BrO_2$, is produced, together with acetophenone. This acid forms needle-shaped crystals (m. p. 130°), soluble in chloroform, petroleum-ether, and hot water. It combines directly with bromine, yielding *hydrotribromatropic acid*, $C_9H_7Br_3O_2$ (m. p. 150°).

Hydratropic acid, $C_6H_5.CH(CH_3).COOH$, formed by the action of sodium-amalgam on atropic acid, is an oily liquid which boils at 264°, and does not solidify at — 20°. The calcium salt forms opaque white needles, containing 2 mols. H_2O, and also glistening transparent needles containing 3 mols. H_2O. A mixture of hydratropic and atrolactic acids is obtained by treating dibromhydratropic acid with sodium amalgam.

Isatropic acid does not form addition-products with bromine or with hydrobromic acid. W. C. W.

Nitrosalicylic Acids and the Isomerism of Benzene Derivatives. By H. Hübner (*Liebig's Annalen*, **195**, 1—55).—α- and β-Nitrosalicylic acids can be prepared by slowly adding salicylic acid to a well cooled mixture of nitric and acetic acids; the product of the reaction is poured into cold water, and the precipitated mononitrosalicylic acids are converted into barium salts. The sparingly soluble β-barium mononitrosalicylate is separated from the salt of the α-acid by recrystallisation from water.

The acids may also be obtained by adding nitric acid to a solution of salicylic acid in glacial acetic acid. In this case the amount of mononitrosalicylic acids formed will not exceed half the weight of the salicylic acid taken, dinitrosalicylic acid, dinitrophenol, and tribromophenol remaining in solution. The mixture of crude acids is dissolved in hot water; on cooling the α-acid separates out. It can be obtained in a state of purity by recrystallisation. The mother-liquors are boiled with barium carbonate, and the mixture of barium salts is separated by repeated recrystallisation.

The α-acid can also be obtained by passing the fumes evolved on heating lead nitrate into an acetic acid solution of salicylic acid, $Pb(NO_3)_2 = PbO + N_2O_4.O$, and $N_2O_4.O + C_6H_4(OH).COOH = NO_2.OH + C_6H_3(OH)(NO_2).COOH$.

I. *α-Nitrosalicylic acid*, $NO_2 : OH : COOH = [5 : 2 : 1]$ (m. p. 228°), previously obtained by Fourcroy and Vauquelin, Chevreul, Buff, Piria, and others, crystallises in long colourless needles, which are soluble in alcohol and in hot water. Ferric chloride imparts a blood-red coloration to its solution. The following salts were prepared:—

Potassium α-nitrosalicylate, $C_6H_3(NO_2)(OH).COOK$, forms small, yellowish-red needles; the *ammonium salt*, $C_6H_3(NO_2)(OH).COONH_4$, forms thick needles; *magnesium nitrosalicylate*, $C_6H_3(NO_2)(OCOO)Mg + 4H_2O$, forms yellow crystals, easily soluble in alcohol and in water. By boiling α-nitrosalicylic acid with barium carbonate, small, yellow, readily soluble, needle-shaped crystals, having the composition $[C_6H_3(NO_2)(OH)COO]_2Ba + 6H_2O$, are obtained, but on boiling the acid with baryta-water, sparingly soluble crystalline scales of $C_6H_3(NO_2)(OCOO)Ba + 2H_2O$ are produced.

The *strontium salt* $[C_6H_3(NO_2)(OH).COO]_2Sr + 5\frac{1}{2}H_2O$, and the

calcium salt, $[C_6H_3(NO_2)(OH).COO]_2Ca + 6H_2O$, form colourless needles, soluble in water.

Zinc nitrosalicylate, $[C_6H_3(NO_2)(OH).COO]_2Zn + 5H_2O$, crystallises in yellow broad needles, soluble in water.

Silver nitrosalicylate, $C_6H_3(NO_2)(OH).COOAg$, is deposited, on cooling the hot aqueous solution, in delicate colourless needles, which are sparingly soluble in cold water. By the action of ethyl iodide on the preceding silver salt, *monethyl nitrosalicylate*, $C_6H_3(NO_2)(OH).COOC_2H_5$, is obtained in long colourless needles (m. p. 93°) which dissolve in alcohol and in ether, but are insoluble in water.

α-Nitrosalicylamide, prepared by the action of alcoholic ammonia on α-monethyl salicylate at 140°, crystallises in long, colourless needles (m. p. 225°), which dissolve in alcohol and in hot water. Potassium, barium, calcium, and lead form crystalline salts with this compound.

α-Amidosalicylic acid, described by Schmitt (*Zeitschr. f. Chem.*, 1864, 323), yields the following derivatives:—*α-Amidosalicylo-sulphuric acid*, $[C_6H_3(OH)(COOH).NH_3]_2SO_4$, colourless prisms, which rapidly turn brown; *α-acetamidosalicylic acid*, $2C_6H_3(OH)(NH.COCH_3).COOH + H_2O$ (m. p. 218°), soluble in alcohol and in water. The magnesium, barium, calcium, and zinc acetamidosalicylates are crystalline salts, soluble in water.

α-Metanitro-orthamidobenzoic acid, $C_6H_3(NO_2)(NH_2)COOH$=[5:2:1]. The product of the action of alcoholic ammonia at 130°, on diethyl nitrosalicylate, is boiled with baryta-water, and the barium salt thus formed is decomposed with hydrochloric acid. Pure α-nitramidobenzoic acid crystallises in slender, needle-shaped crystals (m. p. 263°), which are soluble in alcohol, ether, and in hot water. The acid forms crystalline salts, possessing a yellow colour, soluble in hot water. With hydrochloric acid it forms a crystalline compound, having the composition $C_6H_3(NO_2)NH_3Cl.COOH$, which is decomposed by moisture or by exposure to the air.

On heating *α-nitrosalicylic acid* with quicklime, it yields paranitrophenol (m. p. 114°), which shows that in this acid the nitro-group occupies the para-position with regard to the hydroxyl. By means of the diazo reaction, α-metanitro-orthamidobenzoic acid (m. p. 263°) can be converted into metanitrobenzoic acid (m. p. 141°) which crystallises in needles, soluble in alcohol, ether, and in hot water.

Barium metanitrobenzoate forms sparingly soluble, needle-shaped crystals, containing 4 molecules of water.

Metamidobenzoic acid, $C_6H_4(NH_2).COOH$, obtained by the reduction of the nitro-acid, melts at 173°, after it has been purified by sublimation. The copper salt is obtained as an emerald-green precipitate, on adding copper acetate to barium metamidobenzoate.

II. *β-Nitrosalicylic acid*, $C_6H_3(NO_2)(OH)COOH$ = [3 : 2 : 1], forms large, colourless, needle-shaped crystals, containing one molecule of water, which melt at 125°, whilst the anhydrous acid melts at 144°. It is slightly more soluble in water than the α-acid, and is also freely soluble in alcohol, ether, chloroform, and benzene.

Potassium β-nitrosalicylate, crystallises in long yellow needles, and the *sodium* salt in yellowish-red plates. The *barium β-nitrosalicylates* $[C_6H_3(NO_2)(OH)COO]_2Ba$ and $C_6H_3(NO_2)(OCOO)Ba + 1\frac{1}{2}H_2O$, are

sparingly soluble in water; the former crystallises in thick, golden-yellow needles, and the latter in thick, blood-red needles. The *strontium* salt is freely soluble, the *magnesium* and *lead* salts are but slightly soluble in water. *Silver β-nitrosalicylate* is soluble in hot water; *ethyl β-nitrosalicylate*, $C_6H_3(NO_2)(OH),COOC_2H_5$, is deposited from a hot alcoholic solution in large tabular crystals, which are decomposed by boiling water with formation of alcohol and β-nitrosalicylic acid. *β-nitrosalicylamide*, obtained by the action of alcoholic ammonia on the preceding ether, is a colourless crystalline body (m. p. 145—146°), soluble in alcohol, benzene, water, and chloroform. It forms insoluble salts with barium, calcium, and lead.

β-nitramidobenzoic acid is deposited from an aqueous solution in long, yellow needles (m. p. 204°), freely soluble in alcohol and in ether. The barium, strontium, and calcium salts of this acid containing two molecules of water of crystallisation are sparingly soluble in cold water. *Potassium* and *sodium β-nitramidobenzoates* crystallise in red needles, soluble in water. The *copper* and *lead* salts are insoluble, the *silver* salt is sparingly soluble in hot water. The *ethyl salt* forms yellow glistening scales (m. p. 104°) resembling iodoform in appearance.

β-Nitrosalicylic acid yields orthonitrophenol (m. p. 45°) when heated with quicklime, and by means of the diazo-reaction *β-metanitro-orthamidobenzoic acid* can be converted into metanitrobenzoic acid, which is identical with the acid derived from the α-nitramidobenzoic acid.

The author concludes from the preceding experiments that in a monosubstituted benzene derivative two hydrogen-atoms occupy the meta-position.

Both α- and β-metanitrosalicylic acids, on nitration yield the same *dimetanitrosalicylic acid*, $C_6H_2(NO_2)(NO_2)(OH)COOH = [5:3:2:1]$ (m. p. 173°), which has been described by Cahours (*Annalen*, **69**, 230); by Stenhouse (*Phil. Trans.*, **2**, 413); and by Salkowski (*Annalen*, **163**, 51, and **173**, 40).

The following salts were prepared:—

$C_6H_2(NO_2)_2(OK)CO_2K + H_2O$: dark red needles, soluble in water and in alcohol.

$C_6H_2(NO_2)_2(OH)(CO_2K)$: dark yellow needles, sparingly soluble in water.

$C_6H_2(NO_2)_2(OCO_2)Ba$, and the corresponding calcium and lead salts form sparingly soluble needle-shaped crystals containing three molecules of water. W. C. W.

Polyporic Acid. By C. Stahlschmidt (*Liebig's Annalen*, **195**, 365—372).—In a previous communication (*Annalen*, **187**, 177; and this Journal, 1877, **2**, 620) the author has shown that polyporic acid, obtained from the fungus *Polyporus purpurascens*, dissolves in alkalis, forming a purple solution, and that the purple colour is destroyed by boiling. On the addition of dilute sulphuric acid to the colourless liquid, a precipitate is thrown down, which consists of a mixture of hydropolyporic acid, and a substance having the composition $C_{10}H_9O$. The latter compound is insoluble in water, but dissolves in alcohol, the alcoholic solution having an acid reaction. It melts at 156°.

Hydropolyporic acid, $C_9H_9O_2$ (*sic*), crystallises in colourless needles (m. p. 162°), which are soluble in water and alcohol. The sodium salt, $C_9H_8NaO_2 + 2H_2O$, forms colourless prisms, which effloresce on exposure to the air.

Barium hydropolyporate crystallises in anhydrous quadratic plates, which are sparingly soluble in water. The manganese, copper, cobalt, silver, and lead salts are obtained as precipitates.

By the action of strong nitric acid on polyporic acid, nitropolyporic and benzoic acids and a small quantity of picric acid are formed. Nitropolyporic acid melts at 230°, and is soluble in alcohol and in hot water. By adding potassium chlorate to a boiling mixture of polyporic and hydrochloric acids, three chlorinated compounds are obtained, two of which are insoluble in water, but dissolve in alcohol. The compound $C_9H_7Cl_2O_2$ is soluble in water; it melts at 108°, and at a higher temperature sublimes, forming white needles. $C_8H_6Cl_2O$ is deposited from a hot alcoholic solution in golden needles, which melt at 109°, and sublime without decomposition at a higher temperature. The third substance is a thick, uncrystallisable oil. W. C. W.

Nitrosyl Derivatives. By Girard and Pabst (*Bull. Soc. Chim.* [2], **30**, 531—533).—The crystals of the sulphuric acid chamber, which consist of nitrosylsulphuric acid, $HO.SO_2.ONO$, can be prepared (1) by saturating cold concentrated sulphuric acid with nitrous fumes; (2) by passing sulphurous anhydride into strong nitric acid; and (3) by burning a mixture of 1 part of sulphur with 2 or 3 parts of nitre in a moist atmosphere.

The nitroso-compounds of fluoresceïn and of alizarin are obtained by adding nitrosylsulphuric acid to a solution of alizarin or fluoresceïn in sulphuric acid. By the action of nitrosylsulphuric acid on a solution of aniline or naphthylamine in acetic or in hydrochloric acid, amidoazobenzene and amidoazonaphthalene are produced. On passing nitrosyl chloride, prepared by heating a mixture of sodium chloride and nitrosylsulphuric acid at 85°, into well cooled aniline or toluidine, the hydrochloride of amidoazobenzene, or of amidoazo-orthotoluene is formed.* W. C. W.

Anthraflavone and Anthraxanthic Acid. By A. Rosenstiehl (*Ann. Chem. Phys.* [5], **15**, 245—274).—Anthraflavone is a mixture of three isomerides of alizarin, from each of which an isomeride of purpurine can be derived.

α-Anthraflavone is identical with the metabenzdioxyanthraquinone of Schunck and Roemer (*Ber.*, **10**, 1226). When heated with potash at 135°, it yields *α-oxyanthraflavone*, which was shown to be identical with isopurpurin, by its characteristic absorption spectra, by its insolubility in benzene, by the violet colour of the aqueous solution of its baryta salt, and by a comparison of the acetyl derivatives. Attempts to reduce isopurpurin to α-anthraflavone by the action of phosphorus

* The authors appear to be unaware that they have been anticipated in the use of both nitrosyl chloride and nitrosyl sulphate as means of preparing nitroso-derivatives (see Tilden, this Journal, 1875, **28**, 114; and Stenhouse and Groves, *ibid.*, 1877, **1**, 534).—C. E. G.

and hydriodic acid, or by sodium sulphide and copper, were unsuccessful, only unstable addition-products being obtained.

β-Anthraflavone (the anthraflavic acid of Schunck and Roemer) agrees in every respect with the anthraxanthic acid of Ulrich and Perger (*Ber.*, **9**, 131 and 574). Both substances form bright yellow anhydrous crystals, insoluble in water and benzene, and sparingly soluble in acetic acid and in alcohol. They dissolve in alkalis, forming an orange solution; they are not attacked by potash at 135°, but at 200° they are converted into flavopurpurin.

Flavopurpurin, or *β-oxanthraflavone*, or *Oxanthraxanthin*, is a reddish, crystalline powder, soluble in alcohol and in strong acetic and sulphuric acids. The baryta compound is almost insoluble in water. Reducing agents form with this substance unstable addition-products.

Crude anthraflavone also contains small quantities of anthrarufin (Schunck and Roemer, *Ber.*, **11**, 1176), which yields oxanthrarufin when fused with potash (Liebermann, *Ber.*, **11**, 1613).

α-Anthraflavone is a derivative of oxybenzoic acid, iso-anthraflavic acid is a derivative of anthracene, whilst isopurpurin, β-anthraflavone, and flavopurpurin can be derived from either. Hence it appears probable that in the last three compounds the hydroxyls are distributed between the two benzene nuclei. Purpurin, in which the three hydroxyls are attached to the same benzene nucleus, is converted to purpuroxanthin by reducing agents, whereas these substances merely yield unstable addition-products. W. C. W.

Triphenylmethane and Rosaniline. By E. and O. Fischer (*Liebig's Annalen*, **194**, 242—303).—After referring to the investigations of Hofmann, Liebermann, Zulkowsky, Caro, Rosenstiehl, and others, on the constitution of rosaniline, the authors proceed to describe the results of their experiments on this subject.

Triphenylmethane, $C_{19}H_{16}$, or $C(C_6H_5)_3H$.—When aluminium chloride is gradually added to a mixture of chloroform and benzene, until the evolution of hydrochloric acid ceases, and the product of the reaction is then poured into water, a mixture of diphenylmethane (boiling between 200° and 300°), and triphenylmethane (boiling above 300°) is obtained. *Trinitro-triphenylmethane*, $C_{19}H_{13}(NO_2)_3$ (m. p. 207°) is a crystalline powder, which is sparingly soluble in cold benzene and in cold acetic acid. The acetic acid solution yields *paraleucaniline* on reduction with zinc, and *trinitrotriphenylcarbinol*, $C_{19}H_{12}(NO_2)_3.OH$, on oxidation with chromic acid. The carbinol forms colourless crystals, which melt at 171°, and decompose at a higher temperature. It dissolves freely in benzene and in glacial acetic acid, but is only sparingly soluble in hot alcohol, ether, and in carbon bisulphide. *Triphenylmethane chloride* is most readily obtained in the pure state, by treating the product of the action of phosphorus pentachloride on triphenylcarbinol with six times its volume of petroleum ether, which dissolves out the chloride, leaving the phosphorus chloride undissolved. Pure triphenylmethane chloride begins to decompose at 250°, forming triphenylmethane, and a small quantity of diphenylenephenylmethane, $C_{19}H_{14}$; if the chloride contains carbinol, the formation of the latter pro-

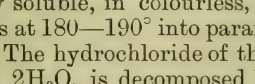
duct is largely increased. Triphenylmethane is also produced by the action of zinc ethyl on the chloride. *Triphenylacetonitril*, $(C_6H_5)_3C.C{\equiv}N$, prepared by heating triphenylmethane chloride with mercuric cyanide, at 150—170°, crystallises in colourless, three-sided prisms, soluble in hot benzene and in hot glacial acetic acid. It melts at 127·5°, and distils without decomposition. On saponification, it yields triphenylacetic acid, $C_{20}H_{16}O_2$ (this volume, p. 326).

Paratolyldiphenylmethane, $C_{20}H_{18}$, obtained from benzhydrol and toluene, and also by the action of phosphoric anhydride on tolylphenylcarbinol and benzene, crystallises in colourless crystals (m. p. 71°; b. p. above 360°), which are soluble in alcohol, wood-spirit, acetic acid, and in benzene. On oxidation, it yields the carbinol, and on reduction of its nitro derivative a mixture of amido-bases is obtained, which form coloured oxidation-products.

Pararosaniline is the name applied by the authors to the colouring matter derived from paratoluidine. Diazopararosaniline hydrochloride, $(ClN_2C_6H_4)_2C(OH)C_6H_4N_2Cl$, forms a yellow crystalline insoluble double salt, with gold chloride, having the composition $C_{19}H_{13}ON_6Cl_6 + 3AuCl_3$. The hydrochloride is decomposed by boiling water with formation of aurin, but its decomposition by boiling alcohol is much more complicated.

Paraleucaniline.—The hydrochloride, $C_{19}H_{19}N_3(HCl)_3 + H_2O$, crystallises in transparent plates. The chloride of *diazoparaleucaniline* has the composition $C_{19}H_{13}(N_2Cl)_3$. A solution of diazoparaleucaniline in sulphuric acid is decomposed by boiling with alcohol, nitrogen and aldehyde are evolved, and triphenylmethane is obtained. As a further proof that pararosaniline is a triamido-derivative of triphenylmethane, this hydrocarbon was converted into paraleucaniline and into pararosaniline by the action of zinc on trinitrotriphenylmethane, or trinitrotriphenylcarbinol.

The formation of a salt of pararosaniline from the trinitrocarbinol takes place in two stages $(NO_2.C_6H_4)_2C(OH)C_6H_4.NO_2 + 9H_2 = (NH_2.C_6H_4)_2C(OH)C_6H_4.NH_2 + 6H_2O$. This compound loses a molecule of water, and combines with an acid to form a salt of the base,



Hydrocyanopararosaniline, $C_{20}H_{18}N_4$, is deposited from hot alcohol, in which it is but slightly soluble, in colourless, oblique prisms. The hydrochloride decomposes at 180—190° into parafuchsine, hydrochloric, and hydrocyanic acids. The hydrochloride of the *diazohydrocyanopararosaniline*, $C_{20}H_{12}N_7Cl_3 + 2H_2O$, is decomposed by boiling with water, forming a compound which is identical with the hydrocyano-derivative Gräbe and Caro obtained from aurin: $C_{19}H_{12}CN(N_2Cl)_3 + 3H_2O = C_{19}H_{12}CN(OH)_3 + 3N_2 + 3HCl$.

Rosaniline.—The authors employ this name to denote the colouring matter derived from orthotoluidine and aniline.

Diazorosaniline hydrochloride, forms double salts with the chlorides of gold and platinum, $(C_{20}H_{13}N_6Cl_3.H_2O) + 3AuCl_3$, and

$$(C_{20}H_{13}N_6Cl_3.H_2O)_2 + 3PtCl_4 + 6H_2O),$$

from which the nitrogen is expelled on boiling with water.

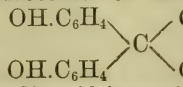
The double chloride of gold and *diazohydrocyanorosaniline*,

$$C_{20}H_{14}(CN)N_6Cl_3 + 3AuCl,$$

evolves only six atoms of nitrogen when boiled with water. This shows that the cyanogen group is combined with a methane carbon atom. The double chloride of gold and *diazoleucaniline* has the composition, $C_{20}H_{15}N_6Cl_3 + 3AuCl_3 + H_2O$.

Tolyldiphenylmethane, $C_{20}H_{18}$, is formed by the decomposition of diazoleucaniline by boiling alcohol. From a saturated solution of the crude product in methyl alcohol, the hydrocarbon separates out as an oil, which slowly solidifies to a crystalline mass, soluble in ether, benzene, and petroleum ether. It melts at 59·5°, and boils above 300°. By the action of chromic acid on the acetic acid solution of the hydrocarbon, *tolyldiphenylcarbinol*, $C_{20}H_{17}OH$, is obtained in colourless crystals (m. p.) 150°, soluble in ether, benzene, and alcohol. The nitro products of this carbinol yield leucaniline on reduction.

Aurin, $C_{19}H_{14}O_3$.—The diazo-compound of the rosaniline obtained from aurin yields triphenylmethane on boiling with alcohol. This confirms the correctness of the formula which Gräbe and Caro propose for aurin,



The name *rosolic* acid is retained for the higher homologue of aurin, $C_{20}H_{16}O_3$. W. C. W.

An Examination of Distilled Essence of Lemon. By W. A. Tilden (*Pharm. J. Trans.* [3], **9**, 654—655).—Two specimens of unadulterated oil of lemons were examined; they both had a sp. gr. of ·852 at 20°; they differed, however, slightly in their action on polarised light, the rotation per 100 mm. for the one being + 58° 34′, and for the other + 59° 16′. The two portions were then mixed and distilled; a few drops of water passed over first, and then the temperature rose directly to 177°; the fractions collected were 177—180° (190 c.c. *a*), 180—185° (52 c.c. *b*), 185—190° (15 c.c. *c*), 190—250° (20 c.c. *d*); a residue amounting to 3 c.c. showed signs of decomposition, water and acetic acid being produced. Distillates *a*, *b*, and *c* were mixed together, heated for some time with sodium, and then again distilled; the whole then came over below 179°. The following substances were recognised:—(1.) A turpentine, $C_{10}H_{16}$, agreeing in general properties with terebenthene. (2.) A terpene, $C_{10}H_{16}$, for which the name *citrene* may be retained, and which constitutes at least 70 per cent. of the crude oil; this terpene differs but slightly from the corresponding terpene of orange as to odour, and it boils at the same temperature, 176°; but it is distinguished by the formation of terpene hydrate when treated with nitric acid and alcohol, whereas hesperidene yields no terpene; citrene treated with strong sulphuric acid yields an inactive hydrocarbon, boiling at about 176°, whilst hesperidene yields viscid products, distilling above 240°. (3.) Cymene, about 6 per cent. (4.) Distillates *c* and *d* consist chiefly of an oxidised compound, $C_{10}H_{18}O$, boiling above 200°, resembling terpinol, except that it is dextrorotatory. (5.) The

viscid residue consists of polymeric hydrocarbons $(C_{10}H_{16})_2$, and also of a compound ether, $C_{10}H_{17}.(C_2H_3O)O$, which is decomposed by heat into $C_{10}H_{16}$, and acetic acid. E. W. P.

Researches on Strychnine. By H. Gal and A. Étard (*Bull. Soc. Chim.* [2], **31**, 98—101).—Finely powdered strychnine, with about ten times its volume of saturated baryta-water, is enclosed in a sealed tube with as little air as possible, and heated for 40 hours at a temperature of 135—140.° The contents are then poured into two volumes of boiling water, the baryta precipitated by a current of carbonic anhydride and filtered off, and the whole evaporated in a flask under reduced pressure until a white crystalline precipitate falls, which is purified by recrystallisation from boiling water.

Thus prepared, the new substance occurs in the form of microscopical needles, which are very slightly soluble in water, but readily so in acidulated solutions; it forms a deliquescent, difficultly crystallisable salt with hydrochloric acid, but with tartaric acid a well-defined acid salt, which crystallises in brilliant prisms. Analysis assigned to the base, which it is proposed to call *dihydrostrychnine*, the formula of strychnine with the addition of two molecules of water, thus: $C_{21}H_{22}N_2O_2 + 2H_2O = C_{21}H_{26}N_2O_4$.

By evaporating the mother-liquors from the first crystallisation, another basic substance was obtained, *trihydrostrychnine*, differing from the above by containing the elements of a third molecule of water, $C_{21}H_{28}N_2O_5$. The two new bases are unalterable in dry air, but are very unstable in solution, they reduce silver nitrate and platinum and gold chlorides, producing at the same time an intense violet-red coloration.

A deficiency of bromine-water produces immediately in solutions of these bases an extremely rich purple coloration, whilst an excess of bromine gives a brown flocculent precipitate, dissolving in hydrochloric acid with a deep carmine-red colour. The coloration disappears under the action of nascent hydrogen, but can be restored by the further addition of bromine. Neither of the bases gives the characteristic reaction of strychnine with potassium dichromate and sulphuric acid.

Trihydrostrychnine differs from Schützenberger's oxy- and dioxystrychnine in that the latter contain in addition to the three molecules of water, one and two atoms of oxygen respectively. J. W.

Contribution to a Knowledge of the Alkaloïds of Ergot. By T. Blumberg (*Pharm. J. Trans.* [3], **9**, 598—600).—The author was unable to prepare ergotinine according to the method of Tanret (*ibid.*, [3], **6**, 522), but obtained it by treating the ergot with ether and 95 per cent. alcohol. The fatty oil obtained by exhaustion with ether, when shaken with water, acidulated with sulphuric acid, and then filtered from the separated fats, was found to contain the alkaloïd. A portion of this filtrate being neutralised with sodium carbonate, was filtered and the precipitate when dissolved in acetic acid yielded a precipitate with potassium-bismuth iodide. Again, the acid aqueous liquid, after being made alkaline, gave up its alkaloïd to ether when shaken

with it, and deposited it in the crystalline state on evaporation. The alkaloïd thus obtained, when treated with two volumes of concentrated sulphuric acid, became first of a rose colour, which changed to deep violet-blue; with Fröhde's reagent, the acid solution assumed a blue colour, which gradually changed to blue-green. Physiologically, ergotinine resembles picrosclerotine in its action on the spinal marrow; both are readily decomposed, and they behave similarly towards sulphuric acid and Fröhde's reagent. Further, the author believes his experiments prove that the ergot resin examined by Ganser was a decomposition-product of ergotinine: that ether withdraws from ergot, besides fatty oil, some portion of the active substance: and that ergotinine was present in Wigger's ergotine. E. W. P.

Action of Potassium Dichromate and Sulphuric Acid on Cholic Acid. By H. Tappeiner (*Liebig's Annalen*, 194, 211—242). —The colouring matter which is contained in crude cholic acid is decomposed to a certain extent by boiling with baryta-water; it can be completely removed by rapidly washing the acid with a very dilute solution of sodium carbonate. Cholesteric, cholanic, lauric, stearic, and several acids belonging to the fatty series are formed by the action of a hot mixture of potassium dichromate and dilute sulphuric acid on pure cholic acid.

Cholesteric acid, $C_{12}H_{16}O_7$, is deposited from the hot filtrate of the crude oxidation-product, in needle-shaped crystals, which are soluble in alcohol, ether, and in hot water. The alcoholic solution is feebly dextrogyrate. The cholesteric acid of Redtenbacher (*Annalen*, **57**, 162), Schlieper (*ibid.*, **58**, 577), and of Gundelach and Strecker (*ibid.*, **62**, 205), is a mixture of cholesteric acid, $C_{12}H_{16}O_7$, and pyrocholesteric acid, $C_{11}H_{16}O_5$. Cholesteric acid is tribasic, and forms amorphous salts. The calcium and barium salts, $(C_{12}H_{13}O_7)_2\,Ba_3$ and $C_{12}H_{14}O_7Ba$, are less soluble in hot than in cold water. $C_{12}H_{13}O_7Ag$ is amorphous, but $C_{12}H_{15}O_7Ag + H_7O$ crystallises in rhombohedrons. The decomposition of cholesteric acid into carbonic anhydride and pyrocholesteric acid, begins at 100°, but takes place more rapidly at 198°. The same change takes place on boiling the acid with sulphuric acid diluted with three times its volume of water.

Pyrocholesteric acid is an amorphous hygroscopic substance (m. p. 108°), which is soluble in water, alcohol, and in ether. The presence of small quantities of this substance deprives cholesteric acid of its power of crystallisation.

Cholanic acid, $C_{20}H_{28}O_6$. When the insoluble portion of the oxidation-products of cholic acid is dissolved in soda solution, and hydrochloric acid added, a precipitate is produced consisting of a mixture of stearic, lauric, and cholanic acids. By treatment with dilute baryta-water, the last-mentioned acid is dissolved out, leaving a residue of barium stearate and laurate. Barium cholanate is precipitated on boiling the solution from which the excess of baryta has been precipitated by carbonic acid. Cholanic acid forms needle-shaped crystals, soluble in alcohol, ether, and in hot water. It dissolves in sulphuric acid, forming a fluorescent solution, which deposits unaltered cholanic acid when diluted. The alcoholic solution is dextrogyrate. At 250°

the acid undergoes no change, but at a higher temperature it melts with decomposition. Cholanic acid forms two series of salts, $C_{20}H_{27}O_6M$ and $C_{40}H_{51}O_{12}M_5$, the latter being a double salt of $C_{20}H_{26}M_2O_6$ and $C_{20}H_{25}M_3O_6$. *Potassium cholanate*, $C_{40}H_{51}O_{12}K_5 + 6H_2O$, crystallises in needles, soluble in alcohol and in water. The three barium salts, $(C_{40}H_{51}O_{12})_2Ba_5 + 10H_2O$; $(C_{40}H_{51}O_{12})_2Ba_5 + 7H_7O$, and $(C_{20}H_{27}O_6)_2Ba + 2H_2O$, are crystalline. The silver and lead salts, $C_{40}H_{51}O_{12}Ag_5$ and $(C_{40}H_{51}O_{12})_2Pb_5$, are amorphous and insoluble. The ethyl salt $C_{20}H_{27}O_6.C_2H_5$ is deposited from an alcoholic solution, in crystals.

W. C. W.

Decomposition-products of Albuminoïds. By S. Kohn (*Chem. Centr.*, 1878, 297—302).—By treating blood-albumin, caseïn, and horn with bromine dissolved in hydrobromic acid, removing excess of bromine by means of platinised lead foil, digesting with platinised zinc, precipitating with alcohol, and purifying by crystallisation, salts are obtained, which give very concordant results on analysis. From analyses of zinc and calcium salts the following formulæ are deduced for brominated acids obtained from (1) blood albumin, (2) caseïn, and (3) horn: (1) $C_{15}H_{27}Br_2N_3O_8$; (2) $C_{15}H_{27}Br_2N_3O_7$; and (3) $C_9H_{17}BrN_2O_7$.

The author regards the acid from blood-albumin as a compound of *Bromodioxyleucine* $C_6H_{12}BrNO_2.O_2$ with *bromotyrosine*, $C_9H_{10}BrNO_3$, water and ammonia; the caseïn acid he regards as a compound of *bromoxyleucine* $C_6H_{12}BrNO_2.O$ with the same bodies; and the acid from horn as a compound of *Bromoxytyrosine* $C_9H_{10}BrNO_3.O_2$ with ammonia and water.

When the zinc salt of the caseïn acid is boiled with caustic baryta, it is decomposed, with production of a compound of bromoxyleucine and baryta, $C_6H_{12}BrNO_2.O.BaO$. Ammonia is evolved during the process, and bromotyrosine is probably formed, but undergoes a secondary decomposition, one of the products being carbonic anhydride. When the zinc salt of the horn acid is similarly treated, two molecules of water are assimilated and the corresponding barium salt is produced, $C_9H_{21}BrN_2BaO_{10}$.

If the filtrates from the zinc salts of the brominated acids of albumin, caseïn, and horn be boiled with caustic lime, and the excess of lime removed as carbonate, crystalline precipitates are obtained, all of which have the same composition, viz., $C_5H_{14}Br_2Ca_2O_6$. When alcohol is added to the caseïn, &c., after bromination, a little carbonic anhydride is evolved, but the greater portion combines with the alcohol, hydrobromic acid, and lime which is subsequently added, to form the above crystalline compound, which may be regarded as

$2C_2H_6O.2HBr.2CaO.CO_2$. M. M. P. M.

Oxidation of Albumin by the Oxygen of the Air. By O. Loew (*Zeitsch. f. Biologie*, **14**, 294—296).—The author succeeded in oxidising albumin by means of a concentrated solution of ammonia and copper filings, changing the air of the vessel frequently and allowing it to remain for four weeks, at the end of which time it gave no precipitate with nitric acid. Oxalate and sulphate of ammonium were

then detected, besides other bodies; but peptone, uric acid, xanthine, leucine, tyrosine, and urea were looked for in vain. E. C. B.

Albuminoïds from Castor-oil Seeds. By H. Ritthausen (*Pfluger's Archiv. f. Physiologie*, **19**, 15—53).—The well expressed and finely powdered seeds were divided into two parts by elutriation with ether. The lighter subsidence from ether (*a*) consisted of well formed crystalloïds and protein granules with comparatively few cell fibres, &c.; the heavier portion of the seeds (*b*) contained besides protein substances, a large quantity of isolated crystalloïds, which appeared under the microscope almost crystalline in character. The residues (*a*) (*b*) respectively were treated (1) with dilute potash, (2) with water at 40—50°, (3) with 10 p.c. solution of sodium chloride, (4) with water containing sulphuric acid, and (5) with solutions of alkaline salts and calcium choride. Finally, the insoluble residues from 2, 3, and 4 were treated with dilute potash.

The albuminoïds were obtained by precipitating the alkaline solutions with sulphuric or acetic acid, the aqueous and sodium chloride solutions with carbonic anhydride, and the acid filtrates with a salt of copper in the manner described by the author (this Journal, 1874, 702).

The results of the numerous experiments made by the author show that the crystalloïds of the seeds of *Ricinus* are soluble in warm water and in solutions of alkaline chlorides and calcium chloride, and contain at least two albuminoïds, one of which is analogous to conglutin, whilst the other differs from it in having more carbon and less nitrogen.

On the other hand the protein granules contain albuminoïds which are less soluble in water and in the alkaline chlorides, the one albuminoïd approximating in composition to conglutin, and the other to mucedin or gluten fibrin. The composition of the predominant crystalloïd and its relation to conglutin is shown as follows:—

	Crystalloïd. p.c.	Conglutin obtained from the yellow lupine. p.c.
C.....	51·31	50·83
H	6·90	6·92
N	18·43	18·33
S	0·97	0·91
O.....	22·39	23·04

The other albuminoïd contained C = 53·3 p.c. and N = 16·07 p.c. In no instance was the albuminoïd altered in composition by being dissolved in potash and reprecipitated by an acid.

In addition to albuminoïds, the seeds of *Ricinus* contain other nitrogenous compounds which contain less nitrogen and are probably glucosides. As glucose was found in all the solutions from which the albuminoïds had been separated, it is inferred either that glucose is a constituent of the proteïn granules or that it had been derived from the glucosides. A. J. C.

Amount of Ash and Soluble Matter in three kinds of Buchu. By H. W. Jones (*Pharm. J. Trans.*, [3], **9**, 673).—Of the three species of buchu it has already been shown that the short-leaved yields 1·21 per cent. of volatile oil, whilst the long-leaved *B. serratifolia* gives only 0·66 per cent. The drug was successively exhausted with dry ether, alcohol, and water, and the resulting solutions were evaporated to dryness, and the residue dried at 113·5°. The ethereal extract contained no essential oil, but chlorophyll and fixed oily matter. In the case of the aqueous extract the amount of mineral matter was deducted. The ash contained a large amount of manganese, and the aqueous extract, a large quantity of mucilaginous matter.

Three Different Samples of Each Species.

	Percentage results.			
	Ash.	Soluble in ether.	Soluble in alcohol.	Soluble in water.
Barosma betulina	4·69	4·62	12·11	13·91
„ „	4·47	4·29	13·96	14·25
„ „	4·40	3·85	8·79	17·91
Barosma crenulata	4·32	5·70	11·26	13·99
„ „	4·01	5·86	15·73	20·72
„ „	5·39	4·01	10·10	17·75
Barosma serratifolia	5·03	4·78	11·57	17·92
„ „	5·55	4·31	9·87	17·05
„ „	5·22	3·91	7·71	22·38

E. W. P.

Physiological Chemistry.

Digestion in the different divisions of the Digestive Canal of the Sheep. By M. Wilckens (*Zeitsch. f. Biologie*, **14**, 281—293).—Criticising Wildt's "Researches on the Stomach of the Ruminantia," the author combats his assumptions (1), that silicic acid is only slightly assimilable on account of the small quantities in which it occurs in the animal organism; and (2), that the progression of the contents of the digestive canal takes place uniformly.

The author then gives several tables which he has drawn up, based on these premises, and shows that supposing them to be true, it follows that in the fourth stomach and in the colon a *secretion* of raw fibres would actually take place. The author concludes that both the above premises are incorrect, and shows further, that the statement of Wildt in regard to the proportion of raw fibres and of albumin cal-

culated to be absorbed in the different divisions of the digestive canal, is quite devoid of morphological or physiological foundation, and is, he considers, incompatible with their histological structure.

E. C. B.

Excretion of Phosphoric Acid by Herbivora. By J. Bertram (*Zeitsch. f. Biologie*, **14**, 335—352).—The author was led to make the researches described in this paper, by observing, in two experiments on castrated goats, that when the albuminous constituents of the food were considerably augmented, a great increase in the amount of phosphoric acid in the urine took place. The urine was alkaline in reaction, and in one case there was a considerable deposit of white crystals of ammonio-magnesian phosphate.

In a series of experiments on a goat, extending over twenty-seven days, in which the animal received daily 13·51 grams of P_2O_5, partly in its hay, and partly as K_2HPO_4, the author found that, after about a week, a regular increase in the phosphoric acid in the urine took place. The following points, amongst others, were noticed in these experiments:—The large doses of potassium phosphate caused the *fæces* to become softer, and their content of water rose to 60 per cent., though there was no diarrhœa, strictly speaking. The watery extract of the fæces gave a marked reaction for phosphoric acid, and contained much potash. The ash contained 15 per cent. of K_2O, whereas, normally, it contains about 2 per cent., showing no doubt that considerable quantities of the phosphate traversed the intestines unchanged. The *urine* was strongly alkaline. Its ash contained considerable quantities of the carbonates of the alkalis. An analysis of the ash showed almost entire absence of lime, and great diminution of magnesia, although the latter earth was still present in considerable quantities in addition to the phosphoric acid, which occurred probably chiefly in combination with magnesia and ammonia. The author concludes that phosphoric acid behaves differently towards lime and magnesia; for, whereas its presence in the urine of herbivora excludes the presence of lime, magnesia may be present at the same time, or may even be in combination with it.

In three different series of experiments in which P_2O_5 was given, it was found that the lime excreted was considerably in excess of that ingested, from which it may be concluded that by excessive doses of phosphoric acid lime is withdrawn from the tissues and fluids of the body in order to combine at least with part of the acid. Hence arises the question, whether phosphoric acid can pass over into the urine if there is a sufficient quantity of lime at its disposal? This question was solved by an experiment in which the animal received, in addition to 800 grams of hay, 9·7 grams of P_2O_5 as PO_4K_2H (total amount of K_2O_5 being 13·27 grams), and 10 grams of calcium carbonate. The phosphoric acid being given at 10 a.m., the lime at 4 p.m., in order that a direct combination of the two in the stomach might be avoided. The results show that on this diet the amount of P_2O_5 in the urine diminished; on the lime salt being discontinued, it gradually rose in quantity, to fall again when the K_2HPO_4 was also omitted.

E. C. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Temperature on the Germination of Seeds. By L. Just (*Chem. Centr.*, 1878, 399).—The general results of the author's investigations, together with those of previous workers, are as follows:—No definite temperature-maximum can be given for the germination of seeds of a particular species. The influence of changes of temperature varies with individual seeds. Maintenance of the maximum temperature during the process of germination causes a slower production of the bud, and retards the entire germinating process. Under favourable conditions the germination of a number of seeds proceeds irregularly: a few begin to germinate quickly; after a time the number in which germination has begun reaches a maximum, and then it gradually decreases until equal to zero. Various seeds exposed to an atmosphere saturated with aqueous vapour lose their power of germination at temperatures dependent on the characters of the individual seeds: as a general rule the higher the temperature the more rapidly is the seed killed. Seeds do not germinate at ordinary temperatures in air saturated with aqueous vapour, unless repeated and considerable fluctuations in temperature occur, resulting in the deposition of dew upon the seeds. Many seeds are deteriorated by exposure to the action of water; the hotter the water the more rapid, generally speaking, is the deterioration. Seeds may, however, be kept unchanged for many hours in water the temperature of which is not much above the maximum at which germination is possible. If immersion in water is accompanied by a diminished supply of oxygen, the seeds are more deteriorated than if oxygen has free access. The drier the seeds, the better are they able to withstand the hurtful action of water; this is not the case with the soft parts of plants (stems, leaves, &c.). Seeds cannot, however, be dried so perfectly as to enable them altogether to resist the action of hot water. If the temperature of the water be raised above 120° to 125°, seeds are generally killed; the temperature at which different seeds are killed varies in different species and individuals.

As a rule, very wet seeds are deteriorated by the action of heat to a greater extent than drier seeds: many seeds, however, when containing a certain definite amount of water, are improved by exposure to a temperature varying from 60° to 70°. The deterioration of seeds which is brought about by the action of water is in many respects analogous to that which seeds suffer under natural conditions as they become older. Deterioration of seeds by increase of temperature is marked chiefly by retardation of the commencement of germination; by an increase in the length of the absolute and also of the relative period of germination; by the maximum germination; occurring at a late period and in an ill-defined manner; and by a decrease in the total germination.

Death of seeds by the action of heat has no connection with the coagulation of the albumin. M. M. P. M.

Presence of an Alcoholic Ferment in Air. By P. Miquel (*Compt. rend.*, **87**, 759—760).—When grape-juice, previously sterilised by boiling, is exposed freely to the air in the vine districts of France, it invariably happens that it enters into fermentation after the lapse of a day or two. In thirty-six experiments, every sample underwent spontaneous alcoholic fermentation. It may be that these numerous cases of apparently spontaneous fermentation are due to the transference of particles of the special vinous ferment from one vessel to another by the numerous winged insects which were not excluded, for it was noticed that when their access was prevented, the must quite as frequently became mouldy instead, and did not ferment. At the same time it is not difficult to show that the alcoholic ferment is conveyed from one spot to another simply by air currents. Eighty-two flasks of about 250 c.c. capacity containing sterilised juice, were opened and immediately closed; in three flasks fermentation set in. Eleven flasks of 1 litre capacity, filled with similar juice, were opened and closed again with great care; the contents of two flasks fermented. Out of twenty flasks filled, for comparison, with filtered air, not one entered into fermentation.

The conclusion is that the alcoholic ferment is in the air, and moreover, that it is more abundant in the vine districts than at Paris, for on repeating these experiments at the latter place, only one case of fermentation was obtained. J. W.

The Succinic Fermentation. By P. Miquel (*Bull. Soc. Chim.* [2], **31**, 101—104).—A solution of impure asparagin rapidly decomposes, becoming converted into ammonium succinate; but a solution of pure asparagin, if properly preserved, can be kept for an indefinite time without decomposition, and the fermentation can be started at any moment by introducing into the solution certain infusorial germs. The author has, after much labour, isolated and examined the special organism which induces this fermentative change; he finds it to be a species of bacterium, which he terms *bacterium commune* on account of the wide distribution of its habitat.

The fermentation of asparagin does not take place in presence of filtered air, nor necessarily even with a limited supply of unfiltered air; in the latter case it frequently becomes mouldy, but the alteration has not the character of a fermentation, it is rather due to phenomena of nutrition similar to those which are observable in saccharine liquids, when the same organisms have access to them. The case is altogether different on the substitution of a few drops of ordinary water for air; the decomposition of the asparagin is then rapid, and the liquor becomes charged with microscopic species of torulæ, bacteria, and vibrios. In about eight days the asparagin had entirely disappeared, its place being supplied by ammonium succinate, a small quantity of ammonium carbonate, a mucous substance, and very small quantities of various products which could not be isolated.

The *bacterium commune* lives, and gives out in the form of carbonic anhydride nearly one-half of the carbon contained in the asparagin, converting the amidogen-grouping into ammonia at the same time. When the transformation is completed, the ferment subsides to the

bottom of the vessel, and the yellow liquid becomes clear and slightly fluorescent; it then possesses an odour recalling that of acetamide.

The bacterium which is the active agent in this fermentation, is said to be present in all ordinary waters, even in rain-water; it is a mobile organism formed of one or at most two articulations, and measuring about $\frac{1.5}{10000}$th of a mm. in length and $\frac{8}{10000}$ mm. in breadth; it is destroyed completely at a temperature of 48—49° if it be maintained constant at that point during two hours. J. W.

The Influence of Chloroform on Nitrification. By O. Hehner (*Chem. News*, **39**, 26).—It has been stated that chloroform prevents nitrification, but this is correct only when chloroform is present in relatively large amounts. To two samples of 8 litres of water containing putrid urine, 5 c.c. and 2 c.c. of chloroform were added respectively; after a month had passed, it was found that the water sample containing 5 c.c. chloroform had remained unchanged, whereas 2 c.c. had been ineffectual to prevent change; in fact, the free ammonia had increased five-fold of that contained in the water to which no chloroform had been added. E. W. P.

Composition of the Ash of Poppy Petals. By C. J. H. Warden (*Chem. News*, **34**, 27).—The composition of the ash, which was of a light grey colour, is given in the table, where A represents the centesimal composition of the ash, as directly determined, and B its composition after deduction of the unessential constituents, carbonic anhydride, sand, and charcoal.

	A.	B.
Ferric oxide, Fe_2O_3	3·0536	3·8647
Aluminium oxide, Al_2O_3	0·9701	1·2278
Magnesium oxide, MgO	4·4311	5·6082
Calcium oxide, CaO	8·4711	10·7214
Potassium oxide, K_2O	32·9926	41·7569
Potassium chloride, KCl	9·7078	12·2867
Sodium chloride, NaCl	0·9537	1·2071
Sulphuric anhydride, SO_3	3·0429	3·8513
Phosphoric anhydride, P_2O_5	4·4331	5·6107
Carbonic anhydride, CO_2	5·4662	—
Silicic anhydride, SiO_2	10·9551	13·8652
Sand	14·5881	—
Charcoal	1·1662	—
	100·2316	100·00

E. W. P.

Analytical Chemistry.

A new Indicator for Use in Acidimetry and Alkalimetry. By H. Borntraeger (*Zeit. Anal. Chem.*, 1878, 459—461).—The advantage of the new indicator is that, unlike litmus, corallin, and phenolphthaleïn, it is not affected by the presence of large quantities of ammonium salts. It cannot, however, be used in presence of free ammonia. It is prepared by leaving some freshly-chopped orange peel in contact for 24 hours with absolute alcohol. The yellow extract is shaken with an equal bulk of ether to separate the essential oil, and the ethereal layer is removed. On adding water, the alcoholic solution yields a colourless liquid in which acids produce no alteration, but which is changed to a beautiful lemon-yellow by alkalis. This indicator can be used only by daylight and for colourless liquids. F. C.

Reduction of Weighings in Air in Chemical Analysis to the Vacuum. By G. F. Becker (*Liebig's Annalen*, **195**, 222—227).—The following table is given for corrections—A for brass weights, B for platinum weights:—

A, for substances whose sp. gr. is between	Correction per gram, error less than $\frac{1}{30}$ milligram.	B, for substances whose sp. gr. is between
27·738 and 11·064	0·000067	—
11·064 „ 6·904	0·000000	51·766 and 13·568
6·904 „ 5·019	0·000067	13·568 „ 7·807
5·019 „ 3·943	0·000133	7·807 „ 5·480
3·943 „ 3·247	0·000200	5·480 „ 4·222
3·247 „ 2·759	0·000267	4·222 „ 3·433
2·759 „ 2·399	0·000333	3·433 „ 2·893
2·399 „ 2·122	0·000400	2·893 „ 2·500
2·122 „ 1·903	0·000467	2·500 „ 2·201
1·903 „ 1·724	0·000533	2·201 „ 1·965
1·724 „ 1·576	0·000600	1·965 „ 1·776
1·576 „ 1·452	0·000667	1·776 „ 1·619
1·452 „ 1·377	0·000733	1·619 „ 1·488
1·377 „ 1·254	0·000800	1·488 „ 1·377
1·254 „ 1·174	0·000867	1·377 „ 1·281
1·174 „ 1·103	0·000933	1·281 „ 1·197
1·103 „ 1·041	0·001000	1·197 „ 1·124
1·041 „ 0·985	0·001067	1·124 „ 1·059
	0·001133	1·059 „ 1·002
	0·001200	1·002 „ 0·950

If the sp. gr. of the substance is greater than 1, no correction is necessary for quantities smaller than 25 milligrams, but if the sp. gr. is greater than 3, corrections are not required for less than 1 decigram. In the present state of chemical apparatus, no correction need be made for variations in temperature or atmospheric pressure.

W. C. W.

Analysis of the Zsadânyer Meteorite. By W. Pillitz (*Zeit. Anal. Chem.*, 1879, 58—68).—The methods of analysis hitherto employed are criticised and those selected by the author given in detail. For the separation of the metals present in the free state, Berzelius employed the magnet; but this method involves the risk of non-metallic constituents adhering to the metallic particles, and, moreover, magnetic iron oxide would accompany the metals. Exner employed cupric chloride solution. Nauckhof dissolved in dilute sulphuric acid, burnt the dried hydrogen evolved and estimated it as water, and subtracted from the total hydrogen the weight which corresponded with the nickel afterwards found in solution, thus obtaining the quantity of hydrogen corresponding with the metallic iron. Piribauer modified this process by determining the volume of the hydrogen evolved, he also purified it from hydrogen sulphide. Nauckhof in another analysis dissolved away the free metals by treatment with mercuric chloride solution, adopting Boussingault's method for dissolving away iron in the determination of the carbon it contains. The author chose the last-mentioned process. He considers the determination of free metals by estimating the hydrogen evolved on treatment with an acid objectionable, because any slight error is much magnified, owing to the very low atomic weight of hydrogen compared with that of the metal. The process of heating in a stream of chlorine involves complicated apparatus. Solution by means of cupric chloride is unobjectionable, but mercuric chloride acts more readily on metals of the iron-groups and excess is more easily removed.

The grey trachytic substance which formed the mass of the meteorite contained many white shining spangles; the outside crust was black, partly smooth and partly rough.

For the purpose of analysis, a considerable quantity was powdered and divided into three parts. The first part (1·5 to 2 grams) was stirred with about twelve times its weight of mercuric chloride and some water in an agate mortar until the metallic fragments disappeared. This mixture was washed into a porcelain dish with half a litre of water and heated for some time nearly to boiling, filtered and washed until free from iron. The *filtrate* was acidified with hydrochloric acid and freed from mercuric chloride by passing sulphuretted hydrogen; the precipitate was rejected; the filtrate was evaporated and filtered from sulphur; and the iron was precipitated by sodium acetate, after oxidation with nitric acid. The iron precipitated required to be four times dissolved and reprecipitated to free it from nickel; it was finally dissolved in hydrochloric acid and precipitated by ammonia. The small quantity of iron precipitated by the concentration of the filtrate was added to the above, and the cobalt, nickel, and manganese were then separated and determined by T. H. Henry's method. (Fresenius, *Quant. Anal.*) The author thinks, however, that the separation of manganese by bromine is preferable. The *precipitate* was dried and transferred to a platinum boat, most carefully avoiding introducing with it any portions or fibres of filter paper; it was then heated in an atmosphere of hydrogen free from oxygen until freed from mercury, and again heated in air or oxygen and the carbon determined as in organic combustions. The residue in the boat was fused

with potassium-sodium carbonate in a crucible carefully covered to avoid the chrome-ironstone being acted upon. The silica was separated as usual and weighed with the chrome-ironstone; it was then removed by covering it with hydrochloric acid in a platinum crucible and passing vapour of hydrofluoric acid into the acid; the residue left was too small to permit of the quantitative separation of chromium and iron, although both metals were easily detected by qualitative tests. In the filtrate from the silicic acid, metals of groups 3 and 4, and calcium and manganese were estimated as usual.

In another portion of the meteorite, the alkalis and the metals precipitated by sulphuretted hydrogen were estimated. Two or three grams, very finely powdered, were mixed with dilute hydrochloric acid and completely decomposed by treatment with hyrofluoric acid; the solution was evaporated to dryness; the residue moistened with sulphuric acid; and after driving off excess of acid the residue was dissolved in hydrochloric acid. The diluted solution, on being treated with sulphuretted hydrogen, gave so small a precipitate that a separation was impossible; it consisted chiefly of copper and tin sulphides. The filtrate can be used for control-determinations of other metals already determined in the first portion, or for the estimation of the alkali metals only. In the latter case, ammonia and ammonium sulphide are added in excess, and the filtrate evaporated after acidifying with acetic acid to decompose ammonium sulphide and separate a trace of nickel sulphide. After filtering, solution of neutral lead acetate is added, then excess of ammonia, and the liquid is boiled to expel the excess of ammonia. Ammonium carbonate is then added in excess, the precipitate filtered and washed with water containing ammonium carbonate; the filtrate is evaporated to dryness after addition of hydrochloric acid in excess. The residue is dissolved in water, and a trace of lead precipitated by sulphuretted hydrogen; the liquid is filtered and evaporated to dryness. The residue gives the weight of the alkali metals as chlorides; they may then be separated by platinum chloride.

Another portion of the powdered meteorite (one or two grams) was fused with twice its weight of potassium nitrate and of sodium carbonate; the cooled mass was dissolved in water, acidified with hydrochloric acid, and after separation of silica, the sulphur was estimated as barium sulphate. The filtrate from the barium sulphate was evaporated to dryness after addition of nitric acid, dissolved in water, acidified with nitric acid, and the phosphorus was precipitated as phosphoric acid by ammonium molybdate, then by magnesium mixed and weighed as magnesium pyrophosphate.

The analytical results obtained were as follows:—The metallic portions amounted to 22·26 per cent., and consisted of Cu + Sn 0·63, Fe 18·23, Mn 1·64, Ni 2·76, Co a trace; the non-metallic elements constituted 78·53 per cent., and contained FeO 11·09, MnO a trace, Al_2O_3 2·23, Cr_2O_3 0·94, MgO 16·46, CaO 3·45, K_2O 4·31, Na_2O 0·31, S 2·64, P 0·45, C 0·21, chrome-ironstone 0·56, SiO_2 34·88. It is worthy of remark that the manganese was almost entirely present in the free state, a trace only of MnO being found; the high percentage of alkali-metals, and especially of potassium, is also noteworthy. The

constituents of the silicates and of the metallic portion are calculated separately to percentages at the conclusion of the paper. F. C.

Estimation of Nitric Acid by Potassium Dichromate. By E. Pfeiffer (*Arch. Pharm.* [3], **13**, 539—544).—The author has slightly altered the process first introduced by Persoz (*Repert. de Chimie Appliquée*, 1861, 253), and his method is as follows:—Potassium dichromate, equal to about four times the weight of the nitrate to be analysed, is heated in a platinum basin to fusion and allowed to cool, when it solidifies to a crystalline mass. About 2 grams of the saltpetre are then weighed out into a platinum crucible, and heated to incipient fusion. After the addition of the weighed dichromate, it is gently heated, the lid being laid on the crucible, but slightly separated from it by a small triangle of platinum wire. After volatilisation of the nitric acid has taken place, the crucible may be more strongly heated, until the mass appears completely fused. Care must be taken to avoid the formation of any chromic oxide, which shows itself as a green coloration on the edge of the crucible: should this have occurred, the analysis is worthless, but it can only occur if the heat has been too suddenly applied at first, or if the nitrous acid had not had sufficient opportunity to escape. The loss of weight is calculated as N_2O_5, unless CO_2 were originally present, when the amount of the latter must be determined by titration. The quantity of CO_2 thus found must be subtracted from the loss of weight, the resulting quantity thus representing N_2O_5 combined with potassium, which has been determined by platinum chloride. If, however, there is an excess of N_2O_5, sodium nitrate is present; but if there is any excess of potassium, this excess must be reckoned first to SO_3, then to chlorine, and any further excess to CO_2. Chlorides and sulphates do not interfere with the analysis. E. W. P.

Estimation of Minute Quantities of Soda in Potassium Nitrate. By F. Castan (*Ann. Chim. Phys.* [5], **15**, 175—179).—From the numerical results detailed in the paper, the conclusion may be drawn that by a process of methodical concentration applied to the mother-liquors, 0·1 gram (that is to say, $\frac{1}{10000}$) of soda existing in a kilogram of potassium nitrate may be determined to less than $\frac{1}{5}$, and consequently that 0·5 gram (that is to say, $\frac{1}{2000}$) may be determined to less than $\frac{1}{25}$ of their absolute values. As for the chlorine, which was only introduced as an indicator, taking into account the facility with which it may be determined, it is obvious that its determination corroborates those conclusions arrived at by the soda determination, as regards the accuracy of the principle which the author announces at the commencement of his paper, that is, when a solution of potassium nitrate in a known weight of water is crystallised, the mother-liquors left by the crystals contain a fraction of the total impurities present, bearing the same ratio to the total impurities as the weight of water contained in those mother-liquors bears to the total weight employed to make the solution. For details of the method the original paper must be consulted. J. M. T.

Alteration of Standard Ammonium Chloride Solution when kept in the Dark. By A. R. Leeds (*Chem. News*, **39**, 17).—Two standard solutions of ammonium chloride were kept in the dark for some months: after that time they were found to be no longer limpid, but to contain a large number of white filaments as well as nitrites. 5 c.c. of the solution were evaporated to dryness with caustic soda and then distilled with 6 grams of pig-iron. The distillate contained 0·03 mgm. NH_3, equivalent to 0·11 mgm. HNO_3, or 0·022 mgm. per c.c. E. W. P.

Valuation of Burned Lime. By J. Stingl (*Chem. Centr.*, 1878, 394—399).—When calcium oxide combines with water to form the hydrate, a contraction in volume occurs; when the solid hydrate is mixed with water, so as to form a stiff mass, a further contraction occurs. The purer the original oxide, the smaller the amount of final contraction, and therefore the larger the volume of lime mortar which can be produced. The author proposes that burned lime intended for use as mortar should be mixed with water to the consistence of a cream, and that the sp. gr. of this cream should be determined. From the data thus obtained, the relative values of various limes could be deduced. In this way the following results were obtained, and are useful as a basis for calculation:—

		Pure oxide.	Lime: From Kimpolung.	Lime: From Krasna.	Lime: From Jesopul.
Percentage of CaO	=	100·00	98·06	97·96	94·68
50 grams mixed with water to the consistence of a thin cream, occupied.....	=	572·3 c.c.	543·8 c.c.	438·4 c.c.	233·5 c.c.
Sp. gr. of this cream....	=	1·1007	1·107	1·145	1·280
				M. M.	P. M.

Estimation of the Available Zinc in Zinc-dust. By R. Fresenius (*Zeitschr. Anal. Chem.*, 1878, 465—468).—The value of zinc-dust used for reducing purposes varies with the quantity of metallic zinc it contains, and not according to the total amount of zinc, since a portion is always present as oxide. Treatment with ammonia yields unsatisfactory results, and the author substitutes for this process the estimation of the quantity of hydrogen evolved by the action of a dilute acid; other metals present with the zinc (*e.g.*, cadmium) are thus valued as zinc. The measurement of the hydrogen being found to be inexact, the gas was burned by passing it mixed with excess of air over glowing copper oxide, and from the weight of water thus formed the weight of metallic zinc present was calculated. The weighed zinc-dust was decomposed in a small flask provided with a safety funnel, through which the dilute sulphuric acid was gradually added, so as to maintain a gentle and regular evolution of the gas; the hydrogen passed through a small cooling apparatus, and then through a sulphuric acid drying **U**-tube into the combustion-tube, in which was first a plug of asbestos, then granular copper oxide, and

finally a longer layer of asbestos and a copper-gauge stopper. The water was absorbed by another **U**-tube charged with sulphuric acid, and this was connected with an aspirator, a calcium chloride tube being interposed to prevent diffusion of aqueous vapour from the aspirator. The contents of the combustion-tube having been first ignited in a stream of dry air, the aspirator is left in action, and the process is commenced by adding a little dilute sulphuric acid; the stop-cock of the safety funnel is left partly open, so as to maintain a slow stream of air through the apparatus; the mixture of hydrogen with excess of air does not permanently reduce the copper oxide. When the acid has dissolved all the zinc powder, the liquid is gently warmed to expel traces of dissolved hydrogen. Every 9 parts by weight of water formed correspond with 32·53 of metallic zinc. The apparatus remains in readiness for another analysis. Zinc, sold as pure, yielded by this process 99·421, 99·32, and 99·40 per cent. of metallic zinc. A sample of zinc-dust gave 91·32 and 91·12 per cent., and another sample 78·43 and 78·14 per cent. of metallic zinc. F. C.

Estimation of Carbon in Cast Iron. By L. Klein (*Zeistchr. Anal. Chem.*, 1879, 76—77).—The author gives results obtained by Classen's modification of Fresenius' and Kolbe's method. Classen removes by means of an improved condenser all acid fumes and almost all moisture, so that only a single sulphuric acid drying tube need be interposed between the flask and the tubes for absorbing the carbonic anhydride. The iron was decomposed by Creath's solution, made by dissolving 340 grams of cupric chloride, and 214 grams of ammonium chloride in 1,850 c.c. of water; 20—25 c.c. of this solution were required for each gram of iron; the decomposition was complete in several hours. The copper and carbon were separated by filtration through asbestos loosely stopping the neck of an ordinary funnel; the residue must be washed until completely freed from chlorine, first with strong hydrochloric acid, and then with alcohol. To this residue chromic acid crystals are added, in the proportion of 6 grams to 2 grams of iron used, and sulphuric acid diluted with half its weight of water is added. The flask containing these substances is then connected with the condenser, and drying and absorption tubes; a slow stream of air is drawn through the whole apparatus from the commencement, to prevent stoppage of the funnel tube. Unless the chlorine is entirely removed from the copper and carbon residue, chromium oxychloride is formed during the distillation and introduces error. The results agreed well with one another and with those obtained by combustion.

F. C.

Detection of Chromates and of Free Chromic Acid. By E. Donath (*Zeit. Anal. Chem.*, 1879, 78—79).—The following tests serve to detect a normal chromate and a dichromate in solution in presence of one another, and chromic acid in presence of chromates. The addition of manganous sulphate solution to a hot solution of a dichromate causes no precipitate; the same salt added to a solution of a normal chromate changes the colour to yellowish-red, and on heating, a heavy dark brown crystalline precipitate forms ($Mn_2CrO_5.2H_2O$). The dichromate gives, when added to a boiling solution of sodium thiosul-

phate, a precipitate or turbidity due to $Cl_4O_9H_2$. Chromic acid separates iodine from potassium iodide; no chromate can decompose the iodide thus. The test is best made by adding solution of potassium iodide and then shaking with carbon bisulphide, the latter being coloured violet if a mere trace of iodine is separated. F. C.

Use of Hempel's Lamp for illustrating Silver Assay as a Lecture Experiment. By Bronner (*Zeit. Anal. Chem.*, 1879, 81—83).—The ordinary heating in a muffle requires at least an hour and a-half, but by the use of the Hempel lamp (*ibid.*, **16**, 454), and by directing on the fused alloy a stream of oxygen, the author reduces the time required to a quarter of an hour. The cupel is supported as a crucible would be, and receives its charge of silver alloy and lead. These are melted in ten minutes, when the cupel is uncovered, and a stream of oxygen directed upon the metallic globule through a metal opening not larger than that of an ordinary blowpipe. The heat produced by the oxidation raises the temperature of the globule, and causes the lead and copper to be entirely removed in two or three minutes. In one experiment the author obtained a fineness of 903 instead of 900. The quantities of gas and of oxygen used are small. F. C.

Estimation of Traces of Lead. By G. Bischof (*Zeit. Anal. Chem.*, 1879, 73—75).—The colorimetric estimation of traces of lead in waters by passing hydrogen sulphide into the liquid, yields very low results in the presence of free hydrochloric or even of free acetic acid; indeed traces of lead are frequently not converted into sulphide at all under these conditions. The author modifies the process by dissolving the water residue, after it has been gently ignited, in as little hydrochloric acid as possible, filtering, and passing hydrogen sulphide for a short time through the filtrate and washings. The liquid is then mixed with slight excess of ammonia, and then again with excess of pure hydrochloric acid. The formation of ammonium sulphide in the liquid secures the conversion of all the lead present into sulphide, which then remains unchanged on again acidifying. In some cases it is preferable to unite the lead sulphide precipitate into lumps by shaking the liquid, to filter this off, and dissolve it in pure strong hydrochloric acid and reprecipitate it as described above for the colorimetric estimation. This proceeding has the advantage of distinguishing lead sulphide from copper sulphide, the latter not dissolving in strong cold hydrochloric acid at all. The standard solution used for comparison is diluted if necessary in the test glass until its colour intensity is the same as that of the test sample. Shaking of the solution after passing the hydrogen sulphide must be avoided, or the colour intensity is apt to be altered by the precipitate uniting into flakes. F. C.

Estimation of Cyanogen in Soda-lyes. By F. Hurter (*Chem. News*, **39**, 25).—The following method for rapidly estimating ferrocyanides in soda is recommended. 100 c.c. of strong soda-lye are oxidised by chlorine or bleaching powder until the whole of the sulphides, &c., are converted into sulphates, and the ferrocyanide into

ferricyanide. This solution, after it has been freed from excess of chlorine and acidified, is titrated with a twentieth normal copper solution, added until a drop of the solution no longer gives a blue colour with ferrous sulphate, but the purple colour of cupric ferrocyanide. The copper solution is prepared by dissolving metallic copper in a minimum quantity of nitric acid, and diluting (3·17 grams Cu are made up to 1 litre, 1 c.c. = ·01013 gram Na_4FeCy_6). Should sodium cyanide be already present, it must first be boiled with ferrous oxide and then oxidised. When thiocyanates are present, the solution should be acidified, and zinc chloride added to precipitate the ferrocyanide. Ferric chloride is then added to the filtered solution, and the resulting coloration is compared with that produced in another solution containing a known quantity of thiocyanate coloured by iron, and diluted until the same tints are obtained. E. W. P.

On the Delicacy of some Reactions for Prussic Acid. By A. Link and R. Mockel (*Zeit. Anal. Chem.*, 1878, 455—459).—A standard solution of prussic acid was prepared, and portions of it were diluted to the requisite strength; 5 c.c. of solution were employed for each experiment.

1. Ammonia was added in slight excess, then silver nitrate, and finally excess of nitric acid. The test was found to be most delicate when made in this way. The reaction gave no result when a dilution greater than 1 : 250,000 was reached.

2. A few drops of rather strong and somewhat oxidised ferrous sulphate solution were added, and the liquid was made alkaline with dilute potash and allowed to stand for five minutes. On adding a slight excess of hydrochloric acid, and warming, the liquid becomes blue or green according to its state of dilution.

The reaction begins to yield a doubtful result when a dilution of 1 : 50,000 is surpassed.

3. Ammonium sulphide was added until the liquid became yellow, then a drop of soda solution to guard against loss of the volatile ammonium thiocyanate, and the liquid was evaporated on the water-bath until it became colourless. Sulphuric acid was added in slight excess, and then some ferric chloride. The reaction gave a distinct coloration up to a dilution of 1 : 4,000,000, beyond which limit the experiments were not continued.

4. A strip of filter paper was saturated with a freshly prepared 4 per cent. extract of guaiacum resin, and when the alcohol had evaporated, it was moistened with a drop of $\frac{1}{4}$ per cent. copper sulphate solution. The deep blue colour appeared with strong solutions, when the paper was suspended over the liquid; in the case of more dilute solutions, the paper was moistened with the liquid; and with the most dilute solutions, 5 c.c. were allowed to slowly trickle over the paper. A distinct coloration was evident up to a dilution of 1 : 3,000,000.

5. Iodide of starch was decolorised only by moderately strong solutions. Its limit of delicacy was about the same as that for the silver reaction. The tests with picric acid, copper sulphocyanide, and uranium nitrate, were not satisfactory with dilute solutions.

The result arrived at is that the most delicate reaction for prussic acid is by formation of ammonium thiocyanate, which slightly surpasses the test with guaiacum copper paper. F. C.

Analysis of Raw Sugars. By E. Laugier (*Compt. rend.*, **87**, 1088—1090).—In order to avoid the errors introduced by drying with access of air, the desiccation of saccharine matters is effected by heating them at about 50° in a current of purified hydrogen or coal-gas. In order to accurately determine the amount of salts, the organic acids in a portion of the substance, double the weight of that taken for the ash, are liberated by adding diluted sulphuric acid drop by drop, and keeping cool. After the mass has been mixed with pounded pumice stone, it is exhausted with ether in an apparatus for continuous distillation. Half of the ethereal solution is added to the ash obtained by igniting the weighed quantity of sugar, when the salts originally present are reconstituted, and may be weighed after drying. The acids in the other half of the ethereal solution are estimated by titration with a standard alkaline solution. R. R.

Estimation of Glycerin in Wine. By C. Neubauer and E. Borgmann (*Zeit. Anal. Chem.*, 1878, 442—451).—Reichardt has simplified Pasteur's method as follows:—The wine extract obtained by evaporation is mixed with slaked lime in slight excess, and evaporated to dryness. On extracting this residue with 90 per cent. alcohol, the succinic acid and sugar remain as insoluble lime compounds, and the alcohol solution when evaporated on a water-bath leaves the glycerin in the pure state.

Reichardt states that in the case of wines which contain potato-sugar, the glycerin requires to be further treated with a mixture of alcohol and ether, in order to separate from it certain dextrinoïd substances whose presence is indicated by the thickening of the impure glycerin on cooling.

Reichardt's numbers are, however, found to be invariably higher than those of Pasteur for pure wines. This the authors believed to be due to impurities present in the glycerin, and they further considered that the impurities separated by alcohol-ether as described above could not resemble dextrin, since they exerted no rotatory effect on polarised light. The substances are probably normal constituents of genuine wine, and therefore are always present in the glycerin separated by Reichardt's method. In investigating the matter experimentally, the authors first proved that a solution of 2 grams of glycerin in 10 c.c. of absolute alcohol gave not the faintest turbidity when mixed with 15 c.c. of ether. A great number of genuine wines were then examined by Reichardt's method, but in every analysis the glycerin was subjected to the purification by alcohol-ether, and the weights of glycerin and of impurity estimated. In every case the treatment with alcohol-ether caused the separation of impurities from the glycerin, the weight separated averaging about one-fifth that of the purified glycerin. The glycerin thus obtained was found, however, to be still impure; it yielded on an average over 2 per cent. of ash, evolved ammonia when heated with soda-lime, and was rendered

slightly turbid on addition of tannin solutions. The nitrogenous substances present were further found to be of different kinds, as after complete precipitation by tannin solution both the precipitate and the filtrate still yielded ammonia when burnt with soda-lime. Of the nature of these azotised bodies, we are as yet quite ignorant.

Reichardt's method was further tested by applying it to the estimation of pure glycerin added in known quantity to wines whose natural glycerin had been previously determined with great care. The results thus obtained were satisfactory, the error being minus, and seldom reaching one-tenth per cent. when quantities of glycerin varying from 0·6 to 2·5 grams were added to 100 c.c. of wine. There is no doubt, therefore, that this method would detect the adulteration of a wine with glycerin to any large extent. On the other hand, wines containing only 0·07—0·08 per cent. of glycerin are suspicious, since pure wines usually contain from 0·7—1·2 per cent., as estimated by the above method. Further, wines which yield 16—17 per cent. of alcohol to 0·12 of mineral matter and 0·299 of glycerin are certainly artificial, and are not produced by the fermentation of the juice of the grape. The authors find it impossible in the present state of our knowledge to fix upon the normal percentage of glycerin which would characterise a genuine wine, or to propose a method for the accurate estimation of glycerin in wine. F. C.

Estimation of Urea by means of Sodium Hypobromite. By G. Hüfner (*Chem. Centr.*, 1878, 303).—The deficit of nitrogen in the determination of urea by Hüfner's original method amounted to 6 per cent. (this Journal [2], **9**, 162). Schleich ([2], **13**, 483) reduced the error to 1 per cent. The author's more recent experiments show that there is always a small deficit in the amount of nitrogen obtained. He gives the following formula for calculating the amount of urea, h, from the volume of nitrogen, v, read off over water: b = barometric reading; b' = tension of aqueous vapour at temperature, t.

$$h = \frac{v(b - b')}{760 \cdot (1 + 0 \cdot 00366t)} \cdot \frac{1}{354 \cdot 3}$$

M. M. P. M.

Estimation of Quinine in Ferri et Quinæ Citras, B.P. By W. Stevenson (*Pharm. J. Trans.* [3], **9**, 673).—The following, which is an adaptation of Teschemacher's method of estimating morphia in opium, is more accurate than that recommended in the B.P. 5 grams of the citrate is dissolved in 50 c.c. of water, and to it is added a slight excess of dilute ammonia: the precipitate is then thrown on a double filter made of two filter-papers, tared in a balance one against the other, by cutting down the heavier, the smaller one to be placed outside to prevent the precipitate getting between the two; this dispenses with using a weighed and dried filter: the precipitated quinine is then washed with distilled water containing one-eightieth its weight of ammonia, ·880, and in which some quinine has been dissolved. By this process all the iron is removed, leaving the whole amount of quinine on the filter, which must first be dried on blotting-paper, and then at 44°. E. W. P.

Quantitative Determination of Theobromine in Cacao and Chocolate. By G. Wolfram (*Dingl. polyt. J.*, **230**, 240—241).—If shelled cacao-beans are to be analysed they are ground up in a hot mortar to a thick paste. 10 grams of this mass, or 20 to 30 grams of chocolate are digested for some time in hot water, treated with ammoniacal lead acetate, filtered whilst hot, and washed with hot water until the acidified filtrate ceases to give a precipitate with sodium phospho-tungstate. The filtrate is treated with caustic soda, and the liquid evaporated to 50 c.c., acidified with sulphuric acid, and the lead sulphate removed by filtration. The filtrate is precipitated with a large excess of sodium phospho-tungstate. The separation of the slimy, yellowish-white precipitate in flakes is facilitated by warming and stirring the mixture gently. After several hours' standing, the liquid is filtered and washed with 6 to 8 per cent. of sulphuric acid. The filter and the precipitate are then treated in a beaker with an excess of caustic baryta, the mixture warmed, the excess of barium hydrate neutralised by means of sulphuric acid, and any excess of the latter thrown down with barium carbonate. The liquid containing the theobromine in solution is filtered whilst hot, and the precipitate washed with hot water. The filtrate is evaporated in a platinum-dish, dried, and weighed. Since, besides theobromine, a small quantity of baryta-salts is always dissolved in the liquid, the alkaloïd is removed by ignition, the residue moistened with ammonium carbonate, evaporated, heated, re-weighed, and the difference between the two weighings calculated as theobromine. D. B.

Determination of Free Acids in Oils. By E. Laugier (*Dingl. polyt. J.*, **230**, 430—432).—The first method mentioned by the author depends on the circumstance that the fatty oils, excepting castor-oil, are almost completely insoluble in alcohol, although it readily dissolves the fatty acids and glycerin. By treating 10 grams of the oil with 50 c.c. of alcohol at 90° four times successively, and evaporating the clear alcoholic solution, the amount of fatty acids and glycerin may be determined, a correction being made for the solubility of the neutral oil in the alcohol. The second method consists in saturating the oil to be investigated with sodium carbonate and extracting with ether. Sodium stearate and palmitate are quite insoluble in ether, which however dissolves the neutral fats and merely traces of sodium oleate.

The assumption that the free acid in fats is oleic acid is said to be erroneous; as a rule a mixture of fatty acids is present which varies according to the character of the fat. D. B.

Simplification of Hehner's Method of Testing Butter. By E. Reichert (*Zeitschr. Anal. Chem.*, 1879, 68—73).—The fat is dried and filtered through cotton wool, and 2·5 grams are weighed in the liquid state into a flask of 150 c.c. capacity; 1 gram of solid potassium hydrate and 20 c.c. of 80 per cent. alcohol are added, and the whole is heated on the water-bath, with constant shaking, until the soap is no longer a frothing, slimy mass: 50 c.c. of water are then added, and as soon as the soap has dissolved, 20 c.c. of dilute sulphuric acid (1 acid to 10 vols.) are poured in and the mixture distilled, a slow

stream of air being constantly passed to avoid bumping. A conical tube should be connected with the flask to avoid sulphuric acid spirting over. If necessary the distillate is filtered into a 50 c.c. flask through a wet filter-paper to separate solid fats. After about 15 c.c. have passed over, the distillate is poured back into the distillation flask, and the distillation is continued until exactly 50 c.c. are obtained. This distillate, which will be quite clear if the process has been slowly conducted, is mixed with four drops of litmus-solution and titrated with decinormal soda-solution. The process yields very constant results when repeated on different portions of the same sample. Many probably unadulterated butters required an average of 14·00 c.c. of soda-solution with a variation of $\pm 0{\cdot}45$ c.c.; any butter requiring less than 12·5 c.c. the author considers adulterated. Cocoa-nut oil, lard, suet, and other adulterants yielded a distillate requiring from 3·7 to 0·25 c.c. only of soda solution. A formula is calculated for approximately determining the percentage of pure butter fats present; this percentage is obtained by subtracting 0·30 from the number of c.c. of soda solution required, and multiplying the number thus obtained by 7·30: the probable error in the percentage thus formed is $\pm$ 0·24 × (number of c.c. −0·30), so that an adulteration exceeding 10 per cent. can be detected with certainty by this process. F. C.

On Testing Butter. By B. E. Dietzell and M. G. Kressner (*Zeitschr. Anal. Chem.*, 1879, 83—85).—A sample of tinned butter was examined by the authors on account of its being suspected to contain oil as an adulterant; the oil had leaked from a crack in the tin and was supposed to be some cheap vegetable oil. The oil had a sp. gr. of 0·9228 at 19°, and solidified at 0—2°; it agreed, therefore, in physical properties with the oil which Chevreul prepared from butter. Its low percentage (85·14) of insoluble fatty acids, as determined by Hehner's method, proved that it was not adulterated with other animal fats. Excluding olive-oil as being too expensive, and linseed-oil on account of its physical properties, determinations of the insoluble fatty acids in palm-oil, rape-seed oil, poppy-oil, and sesame-oil gave an average of 94·4 per cent.: hence the adulteration with both animal and vegetable oils seems impossible. The authors think that palm-oil and sesame-oil are very likely to be added on account of their cheapness and of their suitable properties.

F. C.

Technical Chemistry.

On Cement. (*Dingl. polyt. J.*, **230**, 68—75 and 141—148.)—It is mentioned that hydraulic limes must be divided into hydraulic lime, Roman cement, and Portland cement. The *Vienna Institute of Engineers and Architects* has laid down the following tests for ascertaining the quality of Portland cement:—(1.) The price to be fixed in accordance with the weight. (2.) The volume to remain constant both in the air and under water. (3.) The cement is to be ground as fine as possible.

(4.) Its cementing power to be ascertained by a mixture of cement and sand, the strength of extension being found after seven days and twenty-eight days' setting. As minimum firmness for seven days' setting, 8 kilos.; for twenty-eight days, 12 kilos., to be taken for every square centimeter. The addition of water to be equal to 10 per cent. on the weight of dry substance.

As to the influence of gypsum on cement, it is stated by Schott that the addition of gypsum, burnt or unburnt, retards and perfects the hardening process. It is obvious that the action depends on the quality of the cement. Erdmenger mentions that unburnt gypsum possesses the property of retarding, more or less, the time of setting of cement and of increasing simultaneously its firmness. An excess of gypsum is, however, injurious, in most cases 1 to 2 per cent. is allowable. With regard to the influence of sand on the firmness of cement, it is shown that sand obtained from a sieve containing 120 meshes per square centimeter gives the best results.

Influence of Water on Cement.—The temperature of the water in which cement sets, if between 5° to 22°, does not materially alter the firmness. With regard to the nature of the water used, Michaelis mentions that hard water gives to cement the greatest firmness, but it is not stated whether the hardness is due to the presence of calcium carbonate or of gypsum in the water, or whether the water contains chlorides or nitrates.

Increase of the Firmness of Portland Cement with Increase of the Lime Contents.—Recent experiments have shown that for the best qualities of cement, the most favourable proportion of the acid constituents to the lime is 2·0.

Hardening Theory of Portland Cement.—The following experiment gives some interesting data as to the great variations of firmness which Portland cement shows. A hard-setting cement, still quite new, was taken out of the water after testing and investigated as to its firmness. It was found that after a week's setting the firmness was 18·5 kilos., after four weeks, only 15·7 kilos.; but 40·8 kilos. after further exposure to the air for a week.

Adhesion of Cement-mortar to Brickwork.—As to the adhesive properties of cement, it is mentioned that those varieties which are rich in silica and iron possess the greatest firmness. The direct adhesion of cement to the brick surface scarcely amounts to 1 per cent. of the strength of compression or scarcely to 10 per cent. of the strength of extension.

Increase of the Cementing Power by good Storage.—If Portland cement is stored in a suitable place its cementing power increases, because it becomes finer, more constant in volume, and takes more slowly.

As to the transport of cement in sacks it is stated, that although in Germany cement is not packed in sacks, this has been found to be the most profitable means of conveyance.

Influence of the degree of Fineness on the Properties of Cement.—Delbrück (*ibid.*, **224**, 188) confirms the statement that very finely ground cement allows considerable addition of sand, and yet possesses a high firmness.

Grinding Apparatus for Cement.—Blake's stone-breaker (*ibid.*, **224**, 249) or Renette's mortar-mill (*ibid.*, **227**, 59) is generally adopted

for the grinding process, the product being passed through another mill in which it is reduced to a very fine powder. Finally it is sifted.

D. B.

Analysis of Metallic Fragments obtained from Peruvian Tombs at Ancon (Lima). By A. Terreil (*Compt. rend.*, **87**, 751).—Five specimens of metallic fragments found in tombs at Ancon, in Peru, dating most probably from the middle of the 16th century, were submitted to analysis, on the supposition that the composition of these alloys might throw some light on the metallurgy of Peru at the above date—

	1.	2.	3.	4.	5.
Silver	77·04	33·35	17·27	—	trace
Gold	—	5·42	—	—	—
Copper	7·06	60·83	79·03	65·90	94·35
Zinc	—	—	—	32·04	—
Iron	—	—	—	1·05	—
Chlorine	15·71	0·22	2·31	trace	trace
Oxygen, sulphur, water, arsenic, carbon dioxide	0·19	0·18	1·39	1·01	5·53
Sand	—	—	—	—	0·12
	100·00	100·00	100·00	100·00	100·00

J. W.

Direct Preparation of Wrought Iron and Steel from Iron Ores. (*Dingl. polyt. J.*, **230**, 181—184).—For some time, attempts have been made to introduce practically the direct method of preparing wrought iron and steel from iron ores. Three processes may be distinguished according to the manner of working. (1.) Treating the ores in closed crucibles by external heating. (2.) Flat open vessels made of refractory material, heated at the top and bottom, in which the ore and the coal are placed and the mixture is agitated until reduction sets in. (3.) Rotary cylinders, which are heated either internally or externally. Du Puy's method, which has been to a great extent perfected, is based on the first method of working. On account of the absence of oxidising action, the product obtained improves in quality. As to the chemical part of the process, the operations which take place during the reduction are the combustion of the carbon to carbonic oxide by the absorption of oxygen from the ores; combination of the silica acid and alumina present in the ores with the alkalis added, forming vitreous slag which covers the reduced iron and protects it from oxidation; and finally, the absorption of the total phosphorus present by this slag. The average of fourteen analyses of the Republic ores of Lake Superior gave:—

Metallic Fe, 68·48; P, 0·053; SiO_2, 2·07;

the iron prepared from these ores by the direct process gave:—

Fe.	C.	Si.	S.	P.	Slag.
99·700	0·042	0·021	0·032	0·016	0·185 = 99·996.

D. B.

Working of Mild Steel. By S. Kern (*Chem. News*, **39**, 18).—Mild steel, before being rolled into plates, may be heated to a light welding heat without fear of the ingot crumbling to pieces.

The chief difficulties in obtaining clean Bessemer plates are the innumerable blowholes in the outer parts of the ingots, these blowholes being only masked by rolling; moreover slag scale and sand are also often rolled into the ingot. To avoid these inconveniences, the cheapest way is to weld the steel, and then after re-heating it, roll as quickly as possible. The burning out of the carbon by the heating is but trifling, as the following analyses show:—

Per cent. of carbon.	
Ingots.	Plates.
0·24	0·20
0·24	0·19
0·25	0·21

E. W. P.

Keith's Process for Desilvering and Refining Raw Lead by Electrolysis (*Dingl. polyt. J.*, **230**, 328), a continuation of a former paper (this volume, 288).—This paper refers to Keith's statements respecting the manner in which the residual metallic powder obtained in the above process is worked up. The moist mass is removed from the filters, mixed with the corresponding quantity of sodium nitrate, and dried. It is then brought into crucibles and heated gently; oxide of antimony, arsenious acid, oxides of iron, copper, &c., are formed in the first place, then sodium antimonate, and arsenite. The last-named salts are fusible. Borax renders the slag more readily fusible if oxides of iron and copper are present: at the bottom of the crucible a regulus of gold and silver is deposited. The slag is treated with hot water: the residue contains sodium antimonate and the oxides of copper and iron, whilst the filtrate gives arsenious acid on crystallisation. The antimony may be obtained by mixing the residue with charcoal and heating in the usual manner. When conducted properly, iron and copper should not be reduced by this treatment.

The raw lead used for the experiments gave on analysis:—

Pb.	Ag.	Cu.	Sb.	As.	Traces of Zn, Fe, undetermined substances, loss.	
96·36	0·55	0·32	1·07	1·22	0·48	= 100·00

The refined lead contained 0·000068 per cent. silver, no copper, and only traces of antimony and arsenic. D. B.

Wearing of Steam-boilers. By F. Fischer (*Dingl. polyt. J.*, **230**, 38—45 and 134—141).—It is mentioned that steam-boilers are destroyed through internal or external formation of rust or incrustation, a circumstance which the author thought sufficiently important to investigate more thoroughly. The destruction of the external boiler plates is considered in the first place. The combustion gases which surround the boiler consist mostly of nitrogen, oxygen, steam, and carbonic acid; they also contain carbonic oxide and small quan-

tities of hydrocarbons; if the combustion is conducted badly, and coal and anthracite are used, a considerable quantity of sulphurous acid is formed. Dry boiler plates are not materially injured by the sulphurous acid produced by combustion, but are destroyed in a very dangerous manner if moisture has access, the moist acid combining with the oxygen of the excess of atmospheric air admitted, forming sulphuric acid. Moisture and carbonic acid alone favour the combination of iron with oxygen considerably, and therefore destroy boiler plates, although less readily than sulphurous acid. As to the destruction of the plates in the interior of the boiler, it is stated that the various boiler plates produce galvanic currents with the saline solutions, whereby iron oxide is formed and hydrogen evolved. These currents are said to be produced by the impurities contained in the iron plates of the boiler. The formation of rust is favoured by chlorine-compounds and ammonia, retarded by alkalis; if oxygen is absent, sodium, potassium, barium, and calcium chlorides do not act on iron, although magnesium chloride attacks iron very strongly even in this case; the boiler plates will therefore be attacked more strongly at places where they come in contact with oxygen and carbonic acid, or where they remain in contact with them for some time, *i.e.*, in the cooler parts of the boiler or in the heater. If through a continuous bending to and fro or through alternative expansion and contraction, the plates are continually loosened, so that the moist oxygen is always brought into contact with metallic iron, the rust will quickly penetrate very deeply.

In the second part of this paper the action of fat on boiler plates is more fully described. A large number of black globules, 2 to 3 cm. in diameter, were found in the cylinder of an engine, which consisted of 74·42 per cent. ferrous and ferric oxides, traces of cupric oxide, and 25·14 per cent. organic matter. Ether, acidulated with hydrochloric acid, extracted 18·98 per cent. of a solid brown fat, whilst ether-alcohol without any acid dissolved 11·39 per cent. It was evident therefore that part of the fat was present as an iron soap, the latter being undoubtedly formed by the decomposition of the fat in the cylinder and solution of the iron by the free fatty acids and the combined action of the oxygen contained in the steam. When condensed water is used for feeding purposes, it is advisable to remove the fat by the addition of lime-water, or to saponify with sodium carbonate. It has been further noticed that boilers fed with the water from peat moors are strongly attacked.

To prevent this destructive action, the following precautions should be observed:—Boilers should be constructed so as not to allow the accumulation of air-bubbles or the overheating of the plates at any place. Before using the water, it is best to warm it in open heaters in order to diminish the quantity of oxygen, also to render the water slightly alkaline with soda or lime and to remove as much magnesia as possible.

As to the prevention of boiler incrustation, the author merely corrects a few erroneous statements concerning the use of the so-called magnesia preparation. It is stated by Bohlig (*ibid.*, 212—215) that at temperatures not exceeding 100° the deposited crust formed from

feed waters containing a sufficiency of gypsum is always perfectly free from magnesia; in steam-boilers, however, the whole of the magnesium contained in the water as bicarbonate and sulphate is deposited as magnesium carbonate and more than 3 atoms as magnesia. This statement, however, is not correct, since waters containing calcium and magnesium carbonates merely deposit calcium carbonate on evaporation. Experiments have further shown that no reaction takes place between gypsum and magnesite unless carbonic acid be present. In the analysis of feed waters, this chemist also doubts whether the lime and magnesia, which may be present as bicarbonates, are separated on continued boiling as carbonate. He considers that the magnesium carbonate would thereby be converted into the sulphate, chloride, and nitrate, and the corresponding calcium compounds precipitated as calcium carbonate, and therefore that this method of investigation is incorrect. Fresenius remarks that this statement does not hold good in all cases, as, according to his investigations, the Hunyadi-János bitter-water (p. 366) containing, besides sodium chloride, large quantities of soda and magnesia and a small quantity of lime combined with a large amount of sulphuric acid and very little carbonic acid, deposits on boiling only magnesium carbonate.

In conclusion, a table is given showing the comparative results of purifying water according to the de Haën and Bohlig methods at ten works in Germany, from which it is proved that the treatment with magnesia is neither the cheaper nor the better of the two, most works having given up the use of the magnesia preparation. D. B.

Explosive Mixtures of Air with Combustible Powders. By Berthollet (*Ann. Chim. Phys.* [5], **15**, 240—242).—Attention is drawn to the following facts and observations:—(1.) Clouds of coal-dust raised in mines, by perhaps the combustion of a small quantity of fire-damp, have often served to propagate the inflammation of the air to very considerable distances, burning the workmen and doing terrible injury.

(2.) These effects are especially marked when the air contains traces of fire-damp, the combustible powder making just the addition necessary for the formation of an explosive mixture.

(3.) In absence of any inflammable gas, such powders as flour or very fine charcoal-dust, mixed in certain proportions with air, form explosive mixtures, firing at once on approach of a flame.

About ten years ago a sack of starch was upset at the top of a staircase, and the starch powder diffused in the air becoming ignited by a gas jet produced an explosion. Flour-mill explosions furnish good examples of the above fact (see *Ann. Chim. Phys.* [5], **14**, 144). Similar effects were observed by Berthollet and Carnot on a small scale about the beginning of this century.* It is observed that an

* Abstracts have appeared in this Journal (1872, 930; 1873, 420), in which the explosive combustion of certain powders, as Lycopodium seed, and flour, when mixed with air, is noticed, and the theory given is the same as that of Berthollet. —W.S.

intimate mixture of air with a very finely divided easily combustible powder approaches very nearly the condition of a mixture of an inflammable gas and air. Each grain of powder inflamed, at once surrounds itself with an ignited atmosphere, which communicates the fire to the neighbouring grains. If the grains are sufficiently near each other, this takes place with such rapidity that the gaseous mass expands suddenly with explosive effect. 100 cubic meters of air contain nearly 30 kilos. of oxygen, capable of burning completely 11 kilos. of charcoal powder or 27 kilos. of starch powder. When the mixture of powder and air is not intimate enough to produce an explosion on firing, it may even then be none the less capable of propagating the fire. W. S.

Saki, the Alcoholic Drink of the Japanese. By O. Korschelt (*Dingl. polyt. J.*, **230**, 76—80, 172—181, 229—240, 330—335, and 421—427).—This drink is said to have been known 2,600 years ago. It has been manufactured on a large scale for about 300 years, the largest breweries being those of Ttami, near Osaka. Its preparation is divided into four operations: preparation of *koji;* preparation of *moto;* mashing and fermenting; pressing and clearing.

(1.) *Koji.* The season of the saki-brewing begins in November and ends in February. Rice, which has been previously freed from its husks by pounding, is washed with cold water until the washings become clear. The washed rice is then in the next place macerated in cold water for 24 hours, and then steamed 4 to 5 hours. The soft mass is left to cool on mats, and when cold is treated with tane-koji (tane-seed). Microscopic examination showed that this seed consisted merely of the spores of a fungus. To 4 parts of rice (1 koko = 10 to = 100 sho = 1,000 go = 180·3 lb.) about 2 c.c. of tane-koji were added, and after mixing the whole, the mixture is brought into underground chambers, which are well closed, as the process requires a constant temperature of 20 to 25°. The next morning the rice is worked through by hand, and in the same afternoon a white felt of mycelium will be found to have grown over it. The rice is then taken out of the chambers, put into baskets, which are placed in empty tubs, and water poured over it to one half its volume. After the baskets have been drained for several hours, the rice is spread out on small planks and then brought back to the chambers. The next day it is turned over repeatedly, and the following morning it is taken out. The koji is now ready for use. It may be kept during the cold season for two to three months without changing.

In order to prepare *tane-koji*, the finished koji is placed on boards and brought into the chambers, where it is covered with boards. The next day formation of spores sets in, the felt assuming a yellow colour. The following day the boards are taken out of the rooms and held upside down over an empty plank, the bottom of which is covered with paper. The boards are then tapped gently, the dry spores falling on the paper. From 1 to rice 1 to 1·5 go or 1 to 1·5 p.c. of spores or tane-koji are obtained.

To prepare tane-koji in saki-breweries, the rice is treated with charcoal made from branches of keyakin (*Planera japonica*), tsubaki

(*Camellia japonica*), and nara (*Quercus crispula*) previous to the treatment with tane-koji.

(2.) *Moto.* Steamed rice is mixed with koji and cold water to a thick pap, in the following proportions :—koji 3·6, rice 10, water 11·1. The mass is then agitated, an operation which at first is very difficult, but after two or three days the consistency of the mass changes. It becomes more liquid, owing to the formation of sugar. At the same time fermentation sets in. After six days the mixture is transferred to vessels suitable for warming it. This operation is very slow, four days being necessary to heat the mash to about 13° ; after that the temperature is increased more rapidly, viz., to 20° the next day, and 30—35° the last day. When the fermentation is completed, the mixture is cooled and ready for use. The value of the moto obtained is determined by the differences observed in the taste.

(3.) *Main Process.* For the actual saki-brewing, the following materials are taken :—1 koku of rice, 0·4 koji, 1·1 cold water, and 1·4 moto. These are stirred up in tubs. The fermentation, although slow in the commencement, begins with the formation of sugar, and, at a temperature of about 20°, as a rule, continues for about 17 days. Four days are required for the sugar formation, eleven days for the chief fermentation, and two for the after-fermentation.

(4.) *Pressing and clearing.* The fermented mash is filled into cotton cylinders 60 cm. long and 15 cm. in diameter. These are placed in layers in wooden boxes of various sizes, holding between 150 to 500 bags, and exposed to a pressure which is gradually increased to about 7 t. The saki is collected in the bottom of the box, whence it runs through sieves into clay receivers. From these, it is transferred to clearing vats, where it undergoes after-fermentation, commencing about five or six days afterwards. Unless the product is required for immediate use, this fermentation is allowed to go on ; in either case, however, it is necessary to transfer the saki to the clearing vats so as to remove any solid particles carried through the bags during pressing. Saki of 150 days' storage is said to possess the finest taste. If in the summer it shows signs of turning off, it is *pasteurised* (*ibid.*, **229**, 436). The pressed residues are worked up for alcohol, by distilling them in a cylindrical vat, with perforated bottom, placed over a cast-iron boiler. The residue after distillation is sold as a manure.

In order to become better acquainted with the details of the whole process, the author undertook a large number of analyses with moto-mash, and mash used in the main process at various stages of fermentation. The investigations on moto show that by the fermentation of the former, the concentration of the mash is much greater than by that of any European fermentation (a very thick mash in preparing brandy for instance gives rise to low yields). It is further shown that the solution of the starch continues during the whole process, and even during the fermentation. The acidity of the mash is very slight in the commencement, but increases as the temperature of the mash is raised. At the end of the main fermentation it amounts to 10° of acid. The sum of the unfermented and fermented extract in moto (several weeks old) amounts to 34·86 ; obtained 35·46, showing that the starch is almost completely converted. Analysis further proved that in dilute

mashes, a considerable amount of extract is formed during the first day, whilst in concentrated mashes, the formation of extract is spread equally over a longer period. In the main process, the quantity of extract present in the mash after the complete solution of the starch is equal to 34·9 p.c. against 34·8 p.c. found by experiment. The starch in the main process is therefore dissolved almost completely. In this respect, the saki-breweries surpass our fermentation industries.

Ahlburg has investigated the fungus used for the preparation of saki, and states that it is found only on rice, and when attempts are made to propagate it on other substances, *e.g.*, on potatoes, fruits, &c., it is always mixed largely with *Penicillium* and *Mucorineae*. As to the structure of the fungus, it resembles the genera mucor, aspergillus, botrytis, and eurotium, but differs from these species in various ways. It therefore forms a species of its own, which Alhburg calls "*Eurotium oryzae, Ahlburg.*"

It has already been stated that an addition of yeast to the mash is unnecessary, the moto-mash being prepared only for the purpose of allowing the formation and augmentation of yeast. This formation may be explained in various ways; however, the most probable explanation is that the mycelium of the *Eurotium oryzae*, after the koji has effected the conversion into sugar and the temperature has been increased, splits up into cells, which like the saccharomyces-cells effect the fermentation. With the exception of *Mucor mucedo* and *M. racemosus*, eurotium is the only white fungus the mycelium of which splits up into cells possessing fermentative properties. The yeast of *eurotium*, commonly called *eurotin*, is distinguished from that of mucor by the fact that the action of the latter ceases as soon as the alcohol of the fermented liquid amounts to 3·5 p.c., whilst the eurotin excites liquids containing 15 p.c. or more. Various experiments were made to investigate in what manner the solution of the starch is effected by the substances present in koji, acting as diastase. The results show that a long duration of the mashing increases the yield of extract under all conditions, the best temperature being between 45—50°. As in the germination of corn, so also in the growth of the mycelium, bodies are produced which act on the starch-like diastase. The diastase of eurotium, however, differs considerably from that of germinating corn. Whilst the diastase of barley-malt is as powerful at 65° as at 80°—a circumstance which is explained by the fact that albuminous substances, which are kept in solution at the lower temperature, separate again at the higher temperature—*eurotin* gives the opposite result. The increase of temperature of the mash over 50° is attended by a rapid decrease of the yield of extract. *Eurotin* may be extracted from koji by means of cold water, as diastase is from malt.

In conclusion it is said that with regard to the actual yield of saki, no satisfactory data can be given. The quantity of saki prepared in 1874 was estimated at 6,475,798 hectolitres. D. B.

Aniline-blue (*Dingl. polyt. J.*, **230**, 162—170, 241—245 and 342—351). *Theoretical part.* Aniline-blues are salts of phenylated rosanilines, formed by heating rosanilines under suitable conditions with primary aromatic bases of the aniline type. Three hydrogens of

the rosaniline may be replaced by 1 to 3 phenyl- or tolyl-residues, with a simultaneous loss of 1 to 3 ammonia. Thus mono- di- and tri-phenyl rosanilines are known, which, as bases, are brownish amorphous powders, and as salts, indistinctly crystalline greenish-brown powders, forming red to greenish-blue solutions. The following equations show the reactions of the substituted products :—

(1.) $C_{20}H_{19}N_3 + C_6H_5.H_2N = C_{20}H_{18}(C_6H_5)N_3 + H_3N.$
Rosaniline. Aniline. Monophenylrosaniline.

(2.) $C_{20}H_{18}(C_6H_5)N_3 + C_6H_5.H_2N = C_{20}H_{17}(C_6H_5)_2N_3 + H_3N.$
Diphenylrosaniline.

(3.) $C_{20}H_{17}(C_6H_5)_2N_3 + C_6H_5.H_2N = C_{20}H_{16}(C_6H_5)_3N_3 + H_3N.$
Triphenylrosaniline.

In a similar manner tolylated rosanilines may be prepared. Of the phenyl and tolyl derivatives of rosaniline, the hydrochlorides, sulphates, and acetates are best known analytically. The latter are readily soluble in alcohol, the mono- and di-substituted bodies more than the tri-derivatives, and the tolyl-blues more than the phenyl-blues. The bases and salts are difficultly soluble or insoluble in water, ether, benzene, and petroleum, moderately soluble in methyl, ethyl, and amyl alcohol, and readily soluble in nitrobenzene, aniline, and phenol. Reducing agents convert aniline-blues into the corresponding leucanilines. The preparation of phenylated rosaniline is very imperfect when rosaniline or fuchsine is heated with excess of aniline; the blues are obtained in almost theoretical quantities, however, by adding to rosanilines certain mono-carboxylic acids, *e.g.*, acetic, stearic, benzoic, salicylic acids, and to fuchsines, the anhydrous sodium salts of these acids (especially the acetate and benzoate) in certain proportions. The best yields are not, however, obtained with theoretical quantities; on the contrary, the proportions to be added must be ascertained experimentally, the shade obtained depending also on this circumstance; thus benzoic acid gives blues which dye with a green tinge, whilst acetic acid gives blues with a reddish tinge. The proportion between the quantities of aniline and rosaniline compounds used is of the greatest importance. To maintain the same final results, it is further necessary, that in all cases the materials used should be of the same constitution, and that the time of the reaction and the temperature be the same.

Practical Part.—(1.) *Methyl-blue.* The finer and purified blues are "opal blue;" the blues separated from the melt, "methyl-blue," in opposition to those treated afterwards, are generally called "soluble blue." For the manufacture of a fine blue with green tinge, as it is required in alcoholic solutions for silk dyeing, experience has shown that it is impossible to abandon the use of the rosaniline base; a large excess of pure aniline and benzoic or salicylic acids is also necessary. The salt from which the rosaniline base is prepared, must be equal to the purest fuchsine, the base separated with lime or ammonia being purer than that obtained by soda; it is also preferable to use the salt prepared by the nitrobenzene process, as the smallest quantity of

arsenic has a tendency to carry with it other impurities which interfere with the success of the reaction. The base dissolved in a small quantity of acetic acid should leave no residue after being dried and redissolved, and should show the full intensity of a fine fuchsine. It should also dissolve in ammonia and in alcohol without residue. The aniline used in the operation must be almost pure phenylamine. Between 180° and 182·5°, 97 per cent. should distil over. As to the use of stearic acid, it is stated that, although commercial stearin contaminated with palmitic acid yields a satisfactory product, it is best to use the pure acid. Acetic acid does not give a blue possessing the desired greenish tinge; its recovery also is not practicable. Salicylic and benzoic acids give good results, and although one-third less weight of the former suffices, its cost and the difficulty of recovery render its use less profitable than that of benzoic acid.

For 25 kilos. rosaniline, 250 kilos. aniline, 3 kilos. benzoic acid, a boiler of 500 liters capacity, with agitator, is necessary, the diameter being 85 cm., and height 120 cm. It is heated by means of hot air. The plates are either cast-iron, 3 cm. in thickness, or copper, 2 mm. thick. If iron is used, it is best to line the interior of the vessel with lead. After charging the tube with the above materials, it is fired up gradually to the temperature at which the aniline distils, and kept at this point, otherwise too large a quantity may distil over. The distillate should not contain more than 10 to 15 per cent. of the original substance. Experiments have shown that it is better not to add all the benzoic acid to the mixture at the commencement of the operation, but to retain $\frac{1}{7}$th to $\frac{1}{6}$th of it, which is added when the boiling-point of the mixture has been reached. The result is a stronger evolution of ammonia. When that stage of blueness has been reached at which two samples drawn at intervals are alike in colour, the following more accurate determination is made. A standard alcoholic solution of a standard blue having been prepared, a small quantity of the melt to be tested is put on filter-paper, and the same surface cut out in each case, dissolved in alcohol containing 0·5 per cent. acetic acid, and diluted to the intensity of the standard solution. The differences observed by holding the solutions against homogeneous light, *e.g.*, the light of a gas flame in a dark room, are very slight, and require an experienced eye to judge properly. The heating must be discontinued some time before the melt actually answers to this test; otherwise the shade obtained will not merely differ, but the yield may be affected considerably. While the vessel cools, the quantity of aniline in the distillate is determined. Supposing 30 kilos. have been obtained, then this and the quantity used for phenylating is deducted from the original quantity. From the equation

$$C_{20}H_{19}N_3.H_2O + 3(C^6H^5.H^2N) = C_{20}H_{16}(C_6H_5)_3N_3.H_2O + 3H_3N,$$

we obtain by calculation about 22 kilos. of aniline converted, 52 kilos. have disappeared, and 198 kilos. aniline are left behind. These and the quantity of the colour-base corresponding with the rosaniline must be converted into their hydrochlorides, so as to separate the blue. As only a slight excess of hydrochloric acid of the usual strength (32 per cent.) is required, the quantities for both bases are calculated. After

precipitation, the blue is obtained in a fine powder, the benzoic acid floating on the surface of the solution. The latter is syphoned off, collected, and purified. The precipitate is filtered, the residue pressed in hydraulic presses, digested with an equal weight of hydrochloric acid, diluted with water, filtered, and washed with water, until free from acid and aniline. The moist mass is then dried at 60°, the final product being obtained in the form of a fine brownish-green powder. On cooling, hydrochloride of aniline and a small quantity of blue (residual blue) separate from the filtrates and washings. After neutralising the acid with lime, the mixture is distilled in boilers, so as to recover the aniline.

As to the yield, it may be stated that instead of the theoretical (44·3 kilos.) 40 to 43 kilos. blue are obtained, besides 2 to 4 kilos. residual blue.

When a smaller quantity of aniline is used in the above process, it is necessary to adopt the following treatment, in order to obtain the blue in the same finely divided state. The melt is cooled to 50°, and run into an equal weight of 90 per cent. alcohol. The mixture is treated with hydrochloric acid, filtered when cold, washed with alcohol and hydrochloric acid, and finally with water. By this treatment, however, a portion of the colour is not merely lost, owing to the solubility of the latter in alcohol, but about 3 to 4 kilos. of alcohol per kilo. of blue is used up, which cannot be recovered without difficulty. As a rule, the blue does not require purification, especially when prepared from good raw materials; in some cases it may be boiled with sulphuric acid of 1·3 to 1·4 sp. gr., dissolved in aniline, precipitated with hydrochloric acid as above (on a small scale for analytical purposes), dissolved in alcohol, and precipitated with ammonia so as to obtain the pure base, &c.

The blues with reddish tinge are prepared from fuchsine, sodium acetate, and a small excess of aniline. The operation is the same as that with rosaniline.

Intermediate shades required in commerce are obtained more profitably by mixing the above colours in suitable proportions, than by preparing them direct in the melt.

Soluble Blue.—The salts of the alkalis and alkaline earths of the sulphonic acids of aniline-blue are readily soluble in water. The latter are obtained by dissolving in an excess of sulphuric acid of 1·83 to 1·84 sp. gr., digesting, and finally adding fuming acid. According to the time of action, a mono-, di-, tri- or tetra-sulphonic acid may be obtained. The solubility and the property of combining with metals increases with the quantity of sulphuric acid, the monosulphonic acid forming only 1 series of salts, whilst with the others 2, 3, and 4 series may be obtained. In preparing the soluble blues, the monosulphonic acids and higher-substituted acids must be of great purity.

Alkali-blue.—The preparation of the alkali-sulphonic acid is accompanied by greater difficulties than that of the others, and it is necessary to make certain modifications in the proportions of the weights, in the time, and in the temperature, in accordance with the quality of the methyl-blue operated on. The acids are prepared by introducing the substance into concentrated sulphuric acid, using for all blues, five to

six times the quantity of acid. Finer blues are obtained at a temperature not exceeding 35°; ordinary blues at a temperature not higher than 45°. After complete solution, four to five times the quantity of sulphuric acid, or a mixture of equal parts of common and fuming acid is added, and the whole exposed to a slow action at a moderate temperature. The sulphuric acid is afterwards removed by diluting the mass carefully with twice its weight of water, and filtering; the alkali-sulphonic acid being obtained in a pasty condition. The latter is converted into the soda salt by the addition of a solution of soda to the moist mass. It is best to separate the alkali blue by treating the solution containing the soda salt with sodium chloride, filtering it, treating the residue repeatedly with water, to remove the last traces of sodium chloride, and drying the final product at the ordinary temperature. In dissolving alkali-blues for dyeing purposes, it must be remembered that all metallic compounds of the corresponding sulphonic acids are insoluble in water, excepting those with fixed alkalis; water containing lime, therefore, cannot be used. Alkali-blue should dissolve in five times the quantity of hot distilled water without residue. It should be free from sulphuric acid and chlorine. The best criterion of the purity of the blue, however, is its dyeing properties.

Cotton-blue, or soluble blue, is obtained by treating 1 pt. of methyl-blue with 4 pts. of concentrated sulphuric acid (or at times with 3 pts.). After the solution has been effected, the temperature is raised quickly to 60°, and then slowly to 100°—110°. Sulphurous acid is evolved only when the mixture has been overheated, and has a very disadvantageous action on the product. This gas is more especially evolved when the methyl-blue used for the preparation of the soluble blue was of an inferior quality; in such cases, it is best to use a small quantity of fuming sulphuric acid, when a temperature of 60° to 70° suffices to form the sulphonic acid. The excess of sulphuric acid may be separated from the sulphonic acid by diluting the mass with three to four times the quantity of water and pressing the paste. The latter is treated with the same quantity of water and re-pressed. The residue is then boiled up in a large quantity of water, limed, treated with a slight excess of calcium or barium carbonate, allowed to settle, and the solution filtered and evaporated with a slight excess of ammonia.

The yield of soluble blue on the methyl-blue used is about 125 to 130°, in the case of alkali-blue, and 130—140° in the case of cotton-blue. D. B.

Alizarin-blue. (*Dingl. polyt. J.*, **230**, 433—436.)—This colouring-matter is now brought into commerce in the form of a thin, brownish-violet paste containing 10 per cent. of alizarin-blue. It is almost insoluble in water, difficultly soluble in benzene and alcohol, but dissolves more readily in glacial acetic acid; when heated with the latter it is altered. With concentrated sulphuric acid a red solution is obtained, which when heated and then diluted with water, deposits a blue precipitate, possessing the same dyeing properties as alizarin-blue. A concentrated solution of arsenic acid of 1·9316 sp. gr. dissolves the blue with an orange-red colour. By adding glycerin to this solution, it assumes a fuchsine-red colour, and on heating the solution

and subsequently diluting it, the unaltered colouring-matter separates in the form of blue flakes. This behaviour with acids may serve to recover the alizarin-blue from old pieces of printed goods. Dilute alkalis give greenish-blue or blue solutions; calcium, barium, strontium, and iron salts form greenish-blue lakes, alumina, violet-blue; chromium, violet; and tin, reddish-violet lakes. It may be reduced, like indigo, in an alkaline solution.

Köchlin and Prud'homme give the following formula for a solid blue obtained from this colouring-matter:—0·25 l. alizarin-blue (10 p. c.) are dissolved by means of 0·06 l. soda-lye (1·3298 sp. gr.) and 25 grams zinc-dust, then treated with 0·06 l. glycerin (1·2390 sp. gr.) thickened with 0·75 l. dextrin-water (1,000 grams dextrin in 1 l.) and the mixture printed on cotton. The blue thus obtained is very bright in colour, but not very fast, a better product being obtained by adding a chromium or iron salt to the above colour. These chemists have dyed cotton with alizarin-blue by adding to the bath for 1 pt. of 10 per cent. blue, 1 to 2 pts. of sulpholeic acid in the presence of a slight excess of ammonia. The most profitable manner in which alizarin-blue can be utilised will probably be as steam-blue, it being fixed on the cotton by means of potassium ferrocyanide and chromium acetate; the use of magnesium chloride is also recommended. The blue obtained resists the action of chlorine, but assumes a grey tinge on exposure to sunlight, a circumstance which has greatly interfered with the introduction of this colouring matter in dyeing.

Graebe assigns to alizarin-blue the formula $C_{17}H_9NO_4$. It not only forms salts with bases, but also combines with acids. By treating it with 10 parts of zinc-dust, a base was obtained having the composition $C_{14}H_{11}N$. The latter, although nearly pure, was dissolved in hot dilute hydrochloric acid, the filtrate precipitated by ammonia, and recrystallised from alcohol, a base being obtained which crystallises in laminæ or prisms. It is soluble in alcohol and ether, insoluble in water. Its solutions possess a fine blue fluorescence. The salts of this base have a golden-yellow colour, their solutions showing a deep-green fluorescence. The hydrochloride, $C_{17}H_{11}N.HCl$, forms small prisms when crystallised from water, slender needles when precipitated from an alcoholic solution by means of hydrochloric acid. The sulphate has the composition $C_{17}H_{11}N.H_2SO_4$, and is obtained by precipitating an alcoholic solution of the base with dilute sulphuric acid. It crystallises in needles. By mixing alcoholic solutions of the base and of picric acid, slender needles are obtained of the formula $C_{17}H_{11}N.C_6H_2(OH)(NO_2)_3$; these are insoluble in water, scarcely soluble in alcohol. The platinum-salt, $(C_{17}H_{11}N.HCl)_2PtCl_4$, consists of microscopic needles insoluble in water. D. B.

Action of Chromium Salts in presence of Chlorates. By S. Grawitz (*Compt. rend.*, 87—844).—The author proposes to use potassium dichromate instead of ammonium vanadate in the production of aniline black, inasmuch as ·1 mgram. of the former suffices to convert 125 grams aniline salt per litre into a black, whereas 5 mgrams. of the latter are required. L. T. O'S.

Inactivity of Chromium-compounds in producing Aniline Black as compared with the action of Vanadium Compounds. By G. Witz (*Compt. rend.*, **87**, 1087).—In reference to the last paper the author says that even with 1 milligram of potassium dichromate in presence of potassium chromate, the author could obtain no coloration with 125 grams of aniline chloride dissolved in 1 litre of water, even by the aid of heat. With a solution of the aniline salt of the same strength, and containing 1 to 0·1 equivalent of chlorate of potassium or of sodium, one-fiftieth part of a milligram of vanadium sufficed to develop the aniline black. R. R.

Patents.

1878. *August* 1*st*. No. 3043. J. Duncan, J. A. R. Newlands, and B. E. R. Newlands. **"Improvements in the Treatment of Sugar."**

Raw or low-class sugar containing glucose is agitated for about a quarter of an hour in a close vessel with hot alcohol, in the proportion of about 3 gallons of alcohol to 10 lbs. of sugar. The filtered or decanted alcoholic solution deposits its glucose on cooling, and is reheated and used over and over again until it becomes necessary to distil it in order to separate accumulated water and other impurities. Methyl alcohol or methylated alcohol may be used instead of common alcohol. The sugar deprived of glucose is heated with water as long as adhering alcohol distils over. The use of *heated* alcohol is particularly claimed.

1878. *August* 1*st*. No. 3049. J. Duncan, J. A. R. Newlands, and B. E. R. Newlands. **"Improvement in the Treatment of Saccharine Substances or Compounds."**

These are, the use of alcohol for the following purposes:—

1. To precipitate from aqueous solutions any of the compounds of sugar with lime, commonly called "saccharates, sucrates, or melassates of lime." Two volumes of alcohol are added to one volume of concentrated solution of sucrate. The precipitated lime compounds may be decomposed by carbonic acid or by dilute sulphuric acid.

2. To purify a peculiar compound of lime with sugar and carbonic acid, known as "saccharo-carbonate of lime" (see Johnson's patent, 1867, No. 54, and Murdoch's patent, 1876, No. 240). The lime compound is washed with alcohol until saline and other impurities are removed.

3. To remove the lime salts produced by the action of lime upon saccharine solutions containing more or less glucose. Saccharine solutions are heated with sufficient lime to destroy the glucose present, neutralised with CO_2 or dilute H_2SO_4, and concentrated by evaporation.

1878. *August 3rd.* No. 3073. J. Holliday. **"Improvements in Dyeing and Printing Aniline-black."** (*Communicated by W. S. Grawitz, Paris.*)

The inventor claims "dyeing and printing textile fibres with aniline-black by the action thereon of chromic acid in the presence of chloric or perchloric acid on aniline." As an example, the inventor dissolves in 1,000 parts of water at 90° C., 200 parts starch, 80 parts chlorate of potash, and 130 parts aniline hydrochloride, and when the mixture has cooled, adds one-tenth of a part of potassium or ammonium chromate. This mixture may be used for printing, or the chromic acid or chromate may be applied to the fabric first, and the aniline mixture afterwards.

1878. *August 3rd.* No. 3079. J. Mactear. **"Improvements in the Manufacture of Soda and Potash."**

In order to destroy cyanogen compounds, the inventor adds certain oxidising substances to the mixture of sulphate, coal, and carbonate of lime in the black ash furnace just before withdrawing the charge. The substances selected are calcium, barium, strontium, and magnesium sulphates, and the oxides of iron and manganese. They may be used separately or mixed. When calcium sulphate is used, about 5 parts per 100 of sodium sulphate originally in the charge are sufficient.

1878. *August 7th.* No. 3119. Élisée Cotte. **"Improvements in the Manufacture of certain Explosive Compounds."** (*Communicated by Amadée Lanfrey, of Chartres.*)

The inventor prepares nitrocellulose from "various straws, such as corn, rye, barley, oats, and buckwheat." The straw is boiled with an alkaline carbonate, triturated, washed, and manufactured into a sheet by a paper machine. The sheet is cut up into small pieces, which are immersed for three or four hours in nitro-sulphuric acid, then washed and dried. The little pieces are then steeped in a solution of nitre and dextrin containing charcoal in suspension, drained, and again dried. A "dynamite" may be prepared by mixing the crushed straw nitrocellulose with nitroglycerin. The inventor claims that the straw nitrocellulose is much more stable than gun-cotton, a result which he attributes to the silica contained in the straw, which he considers to play a part analogous to that which it fulfils in dynamite. Corn straw, as containing most silica, is most suitable for the manufacture.

1878. *August 10th.* No. 3166. Henry Brunner. **"Improvements in the Manufacture of Alkali."**

In order to prevent the formation of cyanides in the black ash process, the salt cake and carbonate of lime are first heated to the point of fusion with a portion only (25—75 per cent.) of the necessary quantity of slack. The remaining quantity of slack is then added in one or more portions, and the operation finished as usual. The resulting black ash is practically free from cyanides, and a saving of slack is effected.

1878. *August* 12*th*. No. 3182. R. Lavender. **"Improvements in treating Waste Sulphuric Acid that has been used for pickling Iron Plates and other Articles of Iron or Steel."**

The liquor, which is a solution of copperas, is filtered, evaporated to dryness by superheated steam, the dry residue powdered and introduced into retorts, when it is distilled, the vapours, "consisting principally of sulphurous fumes and acid," being conducted into the ordinary leaden chamber for the manufacture of sulphuric acid. The red oxide of iron left in the retorts is used as a pigment or a polishing powder.

1878. *August* 16*th*. No. 3246. C. F. Claus. **"Improvements in the Manufacture of Sulphide and other Compounds of Zinc, and in the production of Bye-products resulting therefrom."**

This patent relates to the manufacture of a white pigment, consisting of a mixture of zinc sulphide with barium sulphate in various proportions. The bye-products are "caustic baryta, potash, ammonia, and soda," which are separated from sulphides and sulphates in the course of the manufacture.

1878. *August* 17*th*. No. 3252. A. P. Price. **"Improvement in the Preparation and Treatment of Saccharine Substances and Compounds."** (*Communicated by Moriz Weinrich, of Vienna.*)

The object of the invention is to prepare pure "saccharate of lime" from molasses. To the molasses, heated to 85—100° C., dry slaked lime is added in the proportion of ½ cwt. of anhydrous lime to every cwt. of sugar contained in the molasses. After the lapse of 20 hours, the mixture hardens to a brittle mass, which the inventor calls "melassate of lime." This is reduced to a fine powder and agitated with alcohol in a closed vessel provided with mixing mechanism. It is thus brought to a sandy condition, and the lixiviation is carried on with successive doses of alcohol, commencing with 70 per cent. alcohol and finishing with alcohol of 40 per cent. The residue is "purified tribasic saccharate of lime," which may be conducted into the saturating vessels for the treatment of beetroot juice, or may be directly utilised for the production of sugar by decomposition of the "saccharate."

1878. *August* 20*th*. No. 3282. A. A. Croll. **"Improvements in the Manufacture of Sulphate of Alumina."**

Modifications of the process previously patented by the inventor (1877, No. 2884), by which he obtains various qualities of sulphate of alumina in the manufacture of one batch of the salt.

1878. *August* 21*st*. No. 3297. I. Wilkes and T. Johnson. **"Improvements in purifying or refining Copper."**

Some of the crude copper of commerce, such as Chili bars and precipitated copper, contains injurious quantities of arsenic, antimony, and tin. In order to remove these, the inventor uses a mixture of

slaked lime with copper oxide, or peroxide of iron, or peroxide of manganese, preferring them in the forms of copper scale, hæmatite, and natural black oxide of manganese respectively. To a charge of 7 or 8 tons of crude copper, melted in a refining furnace, he adds about 3 cwt. of the lime mixture; the charge is then stirred with a rabble, the temperature of the furnace raised, and the slag skimmed off. This proceding is repeated until the copper has the properties of selected copper. The resulting slags are smelted with copper regulus, and the regulus obtained is rabbled with a mixture of soda ash and copper scale, which oxidises the impurities to arseniate, antimoniate, and stannate of soda, the mixture of which is skimmed off and lixiviated with water, which dissolves out the alkaline salts, and leaves undissolved any copper compound. J. M. H. M.

General and Physical Chemistry.

The light reflected by Potassium Permanganate. By Sir J. Conroy (*Phil. Mag.* [5], **6**, 454—458).—The experiments of Haidinger on this subject are confirmed and extended. The light reflected from the surface of crystals of potassium permanganate, and that from the same substance rubbed on glass, were found to be identical when examined with a dichroiscopic lens. In the spectrum of the former, however, the blue rays are more intense, and the higher bands are more distinctly seen. The following table gives the surface colours at various incidences of light rays, when the light is either unpolarised or polarised in the plane of incidence (A), and when it is polarised perpendicularly to that plane (B), the surrounding media being air, carbon tetrachloride, and carbon bisulphide respectively:—

Angle of Incidence.		Surrounding Medium.		
		Air.	CCl_4.	CS_2.
30°	A.	Pale Yellow	Yellow green	Yellow green.
	B.	„	„	Green.
35°	A.	„	„	Yellow green.
	B.	„	„	Green.
40°	A.	„	„	Yellow green.
	B.	„	Green	Green.
45°	A.	„	Yellow green	Yellow green.
	B.	„	Green	Blue green.
50°	A.	White	Yellow green	Yellow green.
	B.	Pale yellow	Light green	Blue green.
55°	A.	White	Green	Yellow green.
	B.	Yellow with green tinge	Blue green	Blue green.
60°	A.	White	Green	Green.
	B.	Brilliant green	Blue green	Blue green.
65°	A.	White	Green	Green.
	B.	Blue green	Blue green	Blue green.
70°	A.	White	Greenish	Greenish white.
	B.	Blue	„	„
75°	A.	White	—	—
	B.	Metallic with blue shade	—	—

The results of Stokes (*Phil. Mag.*, 1853, **6**, 400) and of Wiedemann (*Pogg. Ann.*, 1874, **151**, 625) as to the spectra of the light reflected by potassium permanganate are confirmed and slightly extended. No definite measurements could be obtained of the amount of displacement of the bands caused by increasing the angle of incidence of a ray which is polarised perpendicularly to the plane of incidence.

M. M. P. M.

Recent Researches on Solar Chemistry. By J. N. Lockyer (*Phil. Mag.* [5], **6**, 161—176).

Theory of Voltaic Action. By J. Brown (*Phil. Mag.* [5], **6**, 142—145).—The author adduces facts which he thinks can only be explained in terms of the chemical theory of voltaic action. Metallic couples when immersed in oxidising electrolytes present phenomena very similar to those obtained from condenser plates arranged in the usual way; but if an electrolyte containing an active ion, such as sulphur, be employed in the first case, new phenomena manifest themselves. If, then, the series of condenser plates, arranged in contact, were brought into an atmosphere containing a suitable sulphur compound, effects should be obtained—if the chemical theory be true—which would place the metals in the same potential order as when immersed in sulphur electrolytes. Such results were obtained by placing plates of copper and iron, well ground together, in an atmosphere of hydrogen sulphide. In air, the light spot of the electrometer moved over 1 cm., the iron being positive, in hydrogen sulphide the spot moved over 3 cms. in the opposite direction. A modification of Sir W. Thomson's experiment was then tried, a bar of aluminium being suspended so as to be movable about an axis perpendicular to the plane of a metal ring, one-half of which was copper and the other iron, the two halves being soldered together. When this arrangement was placed in an atmosphere of hydrogen sulphide, the metallic bar on being electrified turned towards the copper part of the ring, whilst in the ordinary atmosphere, the bar turned towards the iron part of the ring. The author regards his experiments as proving that the difference of potential between two metals is due principally, if not altogether, to the difference of their affinities for one of the elements of some compound gas in the atmosphere which surrounds them.

M. M. P. M.

New Voltaic Element with Constant Current. By A. Héraud (*Compt. rend.*, **88**, 124—126).—The chief feature in connection with the new element is the use of a depolarising agent which shall at the same time contribute to the concentration of the exciting liquid; for this purpose the author employs as the exciting liquid a solution of ammonium chloride, and as a depolariser, mercurous chloride. When the circuit is closed in presence of zinc, ammonium chloride is decomposed thus: $2NH_4Cl + Zn = ZnCl_2 + 2NH_3 + H_2$, the mercurous chloride is reduced by the nascent hydrogen, giving rise to metallic mercury and hydrochloric acid, $Hg_2Cl_2 + H_2 = Hg_2 + 2HCl$. The hydrochloric acid unites with the ammonia, forming ammonium chloride; therefore so long as mercurous chloride is present, ammonium chloride will always be regenerated. The zinc also acts on the mercurous chloride, forming mercury and zinc chloride. Besides these simple reactions, water is decomposed, causing the formation of mercurous chloramide, $Hg_2(NH_2)Cl$, and ammonium zinc oxychloride; the latter deposits itself on the positive plate and thus diminishes the strength of the current and increases the resistance; to prevent this deposition, ammonia, in which the compound is soluble, is added to the solution of ammonium chloride; moreover the zinc plate is suspended a few centimeters from the bottom of the cell by means of an insulated wire; it is thus freed from the crystals which, with the reduced mercury, fall to the bottom of the cell. To prevent the efflorescence of the ammo-

nium chloride and the evaporation of the ammonia, the vessel is closed with a cork smeared with fat and lampblack, and sealed with resin and gutta-percha, or a mixture of collodion and coal-tar. An element which had been in use for 248 days possessed at the end of that time an intensity ·66, as tested by the sine galvanometer; a pile of 9 elements showed at the end of 227 days an intensity 0·73; and at the end of 984 days 0·50, the original intensity being 1. At starting, the resistance of the element was equal to 75·3 m. of telegraph wire, 0·004 m. diameter, and at the end of 12 days it increased to 79·5 m. If the intensity of an element of copper sulphate = 1, then the primitive intensity of the element is 1·4512, and after six months' use the intensity is 1·0749. L. T. O'S.

Electrical Properties of Bees'-wax and Lead Chloride. By W. E. Ayrton (*Phil. Mag.* [5], **6**, 132—141).—This investigation derives its interest from the connection which is shown to exist between specific inductive capacity and the index of refraction for light.

The specific inductive capacity of a wax condenser was measured as it gradually cooled from 90° through the solidifying point: a rise in capacity occurred until the temperature of 60° was reached, after which the capacity diminished. In cooling from temperatures above 80° to that point traces of a slight diminution in capacity were obtained. This is precisely in keeping with the changes known to occur in the index of refraction for light.

The value of the possible objection that the rise in capacity noticed as the wax cooled from 80° to 60° was really due to a slight decrease in the distance between the copper plates of the condenser caused by shrinkage of the solidifying wax, was tested by measuring the conductivity of the condenser at the melting point of the wax, but in no case was there the slightest indication of a rise of conductivity at that point; had the copper plates approached one another when the wax solidified, a rise of conductivity should have been noticed.

Condensers were prepared by pouring melted lead chloride into a carbon box containing a carbon plate separated from the box by pieces of glass: the outer part of the box and the carbon electrode were electrotyped with copper, and copper wires were soldered thereto. A similar condenser was made with a copper box and copper plate, both covered with graphite, and separated from each other by three small pieces of glass. The results were somewhat irregular, but generally it was found that when an electromotive force, not exceeding $1\frac{3}{4}$ volts, was employed, there was an increase in resistance by electrification, as is usually the case with ordinary dielectrics; but that when the electromotive force exceeded $1\frac{3}{4}$ volts, there was a regular or irregular diminution of resistance by electrification, the results being apparently for the most part independent of the nature of the plates of the condenser. As the limiting electromotive force was nearly equal to that required for the decomposition of water, it seems probable that the diminution in resistance was due to a decomposition of the moisture in the lead chloride—which moisture can only be entirely removed with difficulty—and to the action on the chloride of the gases so produced.

M. M. P. M.

On Salt Solutions and Attached Water. By F. Guthrie (*Phil. Mag.* [5], **6**, 35—44, and 105—115).—The author's researches with regard to cryohydrates and cryogens have been continued (*Chem. Soc. J.*, 1877, **1**, 36). The results now given are collected in the following table; I gives the temperature at which the cryohydrate is formed; II, the lowest temperature obtained by means of the salt used as a cryogen; III, the water worth of the cryohydrate, or number of molecules of water held in combination with the molecule of salt:—

Name of Salt.	I.	II.	III.
Barium oxide	0·5°	0·5°	565
Strontium oxide	0·1°	—	1463
Calcium oxide	0·15°	0·18°	1116
Potassium oxide	—	19·2°	—
Potassium permanganate	0·57°	0·52°	608·3
Lead acetate	1·4°	1·7°	82·3
Zinc and potassium sulphate	1·25°	1·01°	167·4
Potassium ferrocyanide	1·7°	1·61°	151·6
Potassium ferricyanide	3·9°	3·9°	19·8—24
Nitrate of urea	4·0°	4·5°	72·83
Potassium oxalate	6·3°	6·2°	17·3
Sodium fluoride	5·63°	3·2°	—
Mercury cyanide	0·45°	0·6°	174
Zinc acetate	5·9°	—	77 p.c.
Sodium thiosulphate	11·0°	10·0°	—
Citric acid	9·2°	9·3°	—
Potassium cyanide	33°	21·1°	—
Sodium oxalate	1·7°	—	—
Cadmium chloride	—	8·3	—
Nickel chloride	—	10·35	—
Sodium citrate	—	11·3	—
Calcium acetate	—	11·8	—
Cobalt chloride	—	15·35	—
Manganese chloride	—	28·0	—
Sodium formate	—	14·3	—
Tannic acid	—	1·5	—
Sulphurous acid	1·5	—	—
Boracic acid	0·7	0·8	—
Arsenious acid	0·5	0·3	—

It will be remarked that the water worth of calcium oxide lies between those of barium and strontium oxides. The cryohydrates of strontium and calcium did not exhibit the opacity generally characteristic of these bodies. The cryohydrate of potassium ferrocyanide is very unstable: when it is allowed to melt, crystals of a yellow salt are often formed, whilst a simultaneous formation of ice and a hydrated ferrocyanide often occurs if a solution of the strength of the cryohydrate is cooled.

Citric acid in common with most other organic acids of high molecular weight has a great tendency to form supersaturated solutions. A saturated solution of citric acid at 0° contains 51·28 per cent. of anhydrous acid.

The first experiments detailed in the second paper were designed to clear up all uncertainty as to the amount of water contained in certain hydrated salts, and to define the conditions under which this water is held in combination. The salt first examined was barium chloride, crystals of which, when dried *in vacuo* at 17° or between sheets of blotting-paper in a screw-press, were proved to contain exactly 2 molecules of water. The salt thus dried and finely powdered was placed in a 2-ounce flask, and dry air was passed over it at a given temperature. It was thus ascertained that at 25° the salt gave up no water, but that at 40° 1 molecule was entirely although gradually removed; apparently this removal takes place at any temperature above 25°. The second water molecule is only given up at temperatures above 60°.

Chromatic Value of other Media than Water.—Most metallic salts are soluble in glycerol (glycerin), and in some cases they combine with this substance in the same way as with water; the molecules may thus be supposed to be "loaded" and should retard the light-wave period or increase its length; that they really do this was proved by solutions of copper sulphate, potassium permanganate, cobalt chloride, and chromium potash alum in glycerol.

Another phenomenon of much interest is noted in this paper. A stiff gelatin jelly saturated with copper sulphate was left exposed to the air, the water partially evaporated, and the salt began to crystallise out; the crystalline masses formed had a bean-like shape, they could be readily picked out of the jelly, and contained 3·5 molecules of water.

F. D. B.

Compressibility of Gases. By L. Cailletet (*Compt. rend.*, **88**, 61—65).—The manometer used by the author in this research, and which serves for the estimation of very high pressures, consists of a soft steel tube 3 mm. in diameter, and about 250 metres long, coiled in a spiral cut on the face of a wooden cylinder 2 m. in diameter; by means of gearing, this cylinder is made to revolve on a vertical axis, which causes the tube to encircle the cylinder or descend into a deep pit. The lower end of the tube is united to a laboratory tube 1·5 m. long and 22 mm. in diameter; in this a piezometer is enclosed, which contains the gas to be experimented with. In order not to exert too great traction on the steel tube, the laboratory tube is suspended by a steel wire 4 mm. in diameter, and graduated every 5 m.; this was wound on a windlass. The well used was 560 m. deep, 1·6 m. in diameter at the mouth, and filled with stagnant water of known temperature. The apparatus and wire were supported by means of a pulley with two grooves fixed at the mouth in the axis of the well.

The apparatus after being exhausted with the Sprengel pump, is filled with mercury, the piezometer is enclosed in the laboratory tube, and the wire and tube simultaneously lowered into the pit, to a depth somewhat less than that actually required, and allowed to assume the temperature of the surrounding medium, when the tube is lowered to the required depth: the pressure is measured by the length of wire unrolled, the pressure of the air also being noted. The apparatus is then brought to the surface, the laboratory tube opened, and the volume occupied by the gas under the abnormal pressure noted, the height to which the mercury has risen being denoted by coating the

internal surface of the piezometer with a thin film of gold, which the mercury dissolves. To avoid errors in measurement, the author employed a large piezometer, which for an increase of 5 m. pressure showed a difference in volume of about 20 divisions. The gas experimented with was nitrogen, and the results are given in detail in the original paper.

In calculating his results, the author has made the following corrections.

(1.) For the temperature of the mercury contained in the tube, which he based on the temperature of the well.

(2.) The elasticity of the wire.

(3.) The external temperature and pressure.

(4.) The temperature of the gas which for pressures, from 1 to 181·985 m., varied from 15° to 17·2°.

From the numbers obtained, it is found that for high pressures nitrogen does not obey Marriotte's law, the compressibility diminishing as the pressure increases. L. T. O'S.

Law of Molecular Volumes. By H. Schröder (*Deut. Chem. Ges. Ber.*, **12**, 119—128).—The determination of the molecular volumes of 15 sodium and 3 lithium salts shows that the stere of each of these metals is 5·90, *e.g.*:—

		As observed.
$\overline{Na_1^4}$	$= 4 \times \overline{5{\cdot}90} =$	23·60
$\overline{Li_1^3}$.....	$= 2 \times \overline{5{\cdot}90} =$	11·80
$\overline{Na_2^4S_1^2O_4^3}$	$= 9 \times \overline{5{\cdot}90} =$	53·1
$\overline{Na_2^4Cr_1^3O_4^3}$	$= 10 \times \overline{5{\cdot}90} =$	59·0
$\overline{Na_2^4Se_1^3O_4^3}$	$= 10 \times \overline{5{\cdot}90} =$	59·0
$\overline{Li_2^3C_1^1O_3^3}$.....	$= 6 \times \overline{5{\cdot}90} =$	35·40
$\overline{Li_1^1N_1^1O_3^3}$.....	$= 5 \times \overline{5{\cdot}90} =$	29·50
$\overline{Na_2^4H_2^1C_2^2O_6^6}$	$= 13 \times \overline{5{\cdot}90} =$	76·7
$\overline{Na_2^4C_1^1O_3^3H_{20}^{15}O_{10}^{10}}$....	$= 33 \times \overline{5{\cdot}90} =$	194·7
$\overline{Na_6^{12}As_2^5O_8^3}$.....	$= 25 \times \overline{5{\cdot}90} =$	147·5
$\overline{Na_1^8P_2^4O_7^7}$	$= 19 \times \overline{5{\cdot}90} =$	112·1
$\overline{Na_1^2P_1^2O_3^3}$	$= 7 \times \overline{5{\cdot}90} =$	41·3
$\overline{Na_2^5W_1^4O_4^3H_2^1O_2^2}$....	$= 17 \times \overline{5{\cdot}90} =$	100·3
$\overline{Na_2^5W_1^4O_4^3}$	$= 12 \times \overline{5{\cdot}90} =$	70·8

Whilst the nitrates of potassium, ammonium, thallium and lithium are isomorphous with arragonite; sodium nitrate, to which the formula $Na_2N_2O_6$ is assigned, is isomorphous with calcite, $\overline{Ca_2^5C_2^2O_6^6}$.

		As observed.
$\overline{Na_2^5N_2^2O_6^6}$.....	$= 13 \times \overline{5{\cdot}90} = 76{\cdot}7 = 2 \times$	38·3
$\overline{Na_1^2Br_1^4H_4^3O_2^2}$	$= 11 \times \overline{5{\cdot}90} =$	64·9
$\overline{Na_1^2I_1^6H_4^3O_2^2}$	$= 13 \times \overline{5{\cdot}90} =$	76·7
$\overline{Na_2^4C_4^1H_6^0O_4^4.H_{12}^9O_6^6}$	$= 33 \times \overline{5{\cdot}90} =$	194·7

The calcium stere was found to be $\overline{5{\cdot}66}$. Since aragonite is isomorphous with strontianite and witherite, its volume molecule must be $\overline{Ca^2_1C^1_1O^3_3} = 6 \times \overline{5{\cdot}66} = \overline{33{\cdot}96}$; similarly the isomorphism of calcite, magnesite, and ferrous carbonate shows that the volume molecule of calcite is $\overline{Ca^2_2C^2_2O^6_6} = 13 \times \overline{5{\cdot}66} = 73{\cdot}6 = 2 \times \overline{36{\cdot}8}$. The volume molecules of the following calcium salts were determined:—

		As observed.
$\overline{Ca^3_1S^2_1O^3_4H^3_4O^2_2}$	$= 13 \times \overline{5{\cdot}66}$	$= \overline{73{\cdot}6}$
$\overline{Ca^3_1S^2_1O^3_4}$	$= 8 \times \overline{5{\cdot}66}$	$= \overline{45{\cdot}28}$
$\overline{Ca^3_1Se^3_1O^3_4H^3_4O^2_2}$	$= 14 \times \overline{5{\cdot}66}$	$= \overline{79{\cdot}24}$
$\overline{Ca^3_1Cl^6_2}$	$= 9 \times \overline{5{\cdot}66}$	$= \overline{50{\cdot}94}$
$\overline{Ca^3_1H^4_4P^4_2O^4_4}$	$= 15 \times \overline{5{\cdot}66}$	$= \overline{84{\cdot}90}$
$\overline{Ca^3_1Ti^2_1O^3_3}$	$= 6 \times \overline{5{\cdot}66}$	$= \overline{34{\cdot}0}$
$\overline{Ca^3_1Ti^2_1O^3_3.Si^2_1O^2_2}$	$= 10 \times \overline{5{\cdot}66}$	$= \overline{56{\cdot}6}$

W. C. W.

Motions Produced by Dilute Acids on some Amalgam Surfaces. By R. Sabine (*Phil. Mag.* [5], **6**, 211—216).—When drops of dilute acid are placed on the clean surface of amalgams of lead, tin, antimony, zinc, or copper, the drops are seen to move about with a more or less jerky motion, the area of the drops undergoing successive irregular contractions and expansions. The author's experiments upon this subject lead him to explain the phenomena noticed as being due to alternate oxidation by the air outside the drop, and deoxidation by electrolysis in the interior of the drop, of a portion of the surface of the amalgam. When the metal amalgamated with mercury is specifically lighter than that metal, the surface of the amalgam consists of mercury in which float innumerable particles of the foreign metal. When the drop of acid comes into contact with such a surface, currents are generated, through the acid, between the mercury and foreign metal.

If the foreign metal be positive to mercury, the latter is deoxidised underneath the drop and therefore cleaned: the adhesion between the drop and this clean surface is less than that between the drop and the original surface, the drop therefore contracts, and in so doing exposes a clean surface of mercury to the air; this again becomes superficially oxidised, whereupon the original state of matters is restored.

In connection with this subject, the author mentions experiments in which a drop of strong nitric acid was placed on the clean dry surface of a rich lead amalgam: the acid spread itself out, the surface underneath assuming a leaden-grey colour, suddenly with a flash the colour changed to white, the colour then gradually deepened until another flash restored the white tint. At the moment of the flash the covered surface became less electropositive. Other phenomena of a similar kind are detailed, and the explanation is offered that while the surface is becoming grey (this change is always gradual), the acid is attacking lead, and when the surface suddenly becomes white, the acid is attack-

ing mercury. The apparent passivity of the mercury for some time is explained by supposing that at first a thin stratum of lead nitrate is formed which tends to protect the mercury from the action of the acid, but that the acid soon diffuses through this stratum and attacks the mercury, until the action is stopped by the accumulation of mercury nitrate, whereupon the electropositiveness of the lead is re-asserted, a fresh diffusion ensues, and the phenomena are repeated.

M. M. P. M.

Thermal Effect of the Walls of Closed Vessels on the Contained Gases. By A. Witz (*Ann. Chim. Phys.* [5], **15**, 433—529).—This paper deals with the important question of the thermal effect which the walls of a vessel such as a cylinder of a steam engine exert on the gases contained therein. The author, who is practically engaged in the construction of steam engines, was led to study the effect of steam jackets on the cylinder, and has found that the great economy of steam obtained by the use of these jackets is due entirely to the action of the cylinder walls. This action he considers to be complex, as it is a function of the physical properties of the gases and the enclosing vessel. From a purely theoretical point of view, this investigation is of much greater interest to the physicist than to the mechanical engineer. The author has studied both the theoretical and practical issues of this question, and for this purpose has divided his work into two parts, (1) the theoretical and experimental investigation of the effect of enclosing walls on gases, and (2) a discussion of some of the prevailing opinions on the part which the walls of cylinders play in thermic motors elucidated by the theoretical conclusions arrived at in the first part.

In the substance of his paper, the author enters into a full description of the methods by which he ascertains the coefficients necessary for the construction of the formulæ from which he draws his conclusions. He considers that the thermal effect of the enclosing walls of vessels on gases which they contain is due to a double action of contact and radiation.

The action of contact is predominant when the gas acted upon is far from its point of liquefaction, and at a pressure of at most 900 mm. (for air), and when the gas is in a state of agitation similar to that which accompanies its expansion or its passage from one reservoir into another.

Under these conditions the rate of heating of the gas may be represented by an expression of the form—

$$V = m(\alpha + \beta\epsilon)\epsilon P^{-0\cdot55}$$
$$V = m'\epsilon^{1\cdot216}P^{-0\cdot55}$$

When P is the pressure and ϵ the excess of temperature of the walls over that of the gas, the time necessary for the temperature to pass from ϵ_1 to ϵ_2 is—

$$X = \frac{\log. \frac{\epsilon_1(\alpha + \beta\epsilon_2)}{\epsilon_2(\alpha + \beta\epsilon_1)}}{m\alpha \log \epsilon}$$

If the artificial movement of the molecules is diminished, or the

mobility of the molecules themselves decreases, the action of radiation is at once observed, this action increasing rapidly with the pressure and the nature of the gas. The phenomena now become more complicated, and are no longer capable of simple mathematical expression; the rapidity of cooling is greater than the rate of heating. The thermal effect of walls is considerable during the expansion of gases, no matter how rapidly the expansion may take place. J. M. T.

Accuracy of Thermochemical Results. By J. Thomsen (*Deut. Chem. Ges. Ber.*, **11**, 2183—2188).—In this, as also in another paper (*J. pr. Chem.* [2], **17**, 166), the author replies to the attacks of Berthelot (*Compt. rend.*, **77**, 24, *Ann. Chim. Phys.*, **5**, 14, 445), who questions the accuracy of the author's observations. P. P. B.

Heat of Formation of Metallic Sulphides. By J. Thomsen (*J. pr. Chem.* [2], **19**, 1—21).—The author's previous papers contain the data necessary for calculating the heat of formation of soluble metallic sulphides: the only step wanting for that of the insoluble sulphides was the determination of the heat evolved in the decomposition of metallic salts by sodium sulphide in aqueous solution, and this is dealt with in the present paper.

Normal sulphides ($R_2.SAq$) do not exist in aqueous solution, since they split up into hydrates and sulphydrates, but their heat of formation is given in the following table:—

Soluble Sulphides.

Reaction.	Evolution of heat.	Reaction.	Evolution of heat.
$K_2.S.Aq$	113,260 units	K.S.H.Aq	65,100 units.
$Na_2.S.Aq$....	103,970 ,,	Na.S.H.Aq....	60,450 ,,
$Li_2.S.Aq$	115,220 ,,	Li.S.H.Aq	66,080 ,,
Ba.S.Aq	107,130 ,,	$Ba.S_2.H_2.Aq$..	124,160 ,,
Sr.S.Aq	106,650 ,,	$Sr.S_2.H_2.Aq$..	123,680 ,,
Ca.S.Aq	98,330 ,,	$Ca.S_2.H_2.Aq$..	115,360 ,,
$H_2.S.Aq$	9,260 ,,	$Mg.S_2H_2.Aq$..	114,800 ,,
		$NH_3.S.H_2.Aq$..	23,890 ,,

Insoluble Sulphides.

Reaction.	Evolution of heat.	Reaction.	Evolution of heat.
$Mn.S.nH_2O$	46,370 units	$Tl_2.S$	21,630 units.
$Zn.S.nH_2O$	41,550 ,,	Pb.S	20,400 ,,
$Cd.S.nH_2O$	33,950 ,,	$Cu_2.S$	20,240 ,,
$Fe.S.nH_2O$	23,750 ,,	Hg.S	16,860 ,,
$Co.S.nH_2O$	21,710 ,,	$Ag_2.S$	5,310 ,,
$Ni.S.nH_2O$	19,370 ,,	H_2S	4,510 ,,

A comparison of the heat of formation of oxides with sulphides shows that the affinity of metals for sulphur is less than it is for oxygen. In the case of the alkalis and alkaline earths, the difference is constant, and amounts on the average to 51,270 units for the substitution of an atom of sulphur by oxygen, *e.g.*, $K_2.O.Aq = 164,560$, $K_2.S.Aq = 113,260$, difference = 51,300.

This constant difference is a necessary consequence of the equality of the heat of neutralisation of the alkalis and of the alkaline earths, and this equality causes a constant difference in the heat of formation of the oxides, and the chlorine, bromine, and iodine compounds of the corresponding metals in aqueous solution.

The heat of formation of thallium sulphide in aqueous solution would be 12,140 units, as the heat of solution of this sulphide is $-33,770$ and $Tl_2.S = 21,630$. Whilst the heat of formation of soluble sulphides is less by a constant number than that of the corresponding oxides; in the case of the insoluble sulphides the differences varies from 48,000 units for manganese to 590 units for silver.

The action of sulphuretted hydrogen on metallic solutions is shown in the following tables, in which it is seen that heat is absorbed in the case of those which are not precipitated and evolved in the case of those that are: this agrees with the fact that, as a rule, a reaction takes place in aqueous solutions only when heat is evolved.

R.	$R.S.nH_2O.$	$R.O.N_2O_5.Aq.$	$RN_2O_6Aq.SH_2Aq.$
Mn	46,370	117,670	−12,200
Fe.....	23,750	89,620	− 6,770
Ni.....	19,370	83,370	− 4,900
Co.....	21,710	84,490	− 3,680
Zn.....	41,550	102,510	− 1,860
Cd.....	33,950	86,000	+ 7,050
Pb	20,400	68,070	+11,430
Tl_2.....	21,630	66,540	+14,190
Cu.....	9,730	52,410	+16,420
Hg	16,860	37,320	+38,640
Ag_2.....	5,310	16,780	+47,630

The same result obtains in the case of all other salts which have the same heat of neutralisation as nitric acid. Weaker acids, such as the acetic, the heat of neutralisation of which for these bases is less than that of nitric acid, exhibit a stronger positive heat of decomposition. Zinc is an exception, the evolution of heat being positive, and this corresponds with the fact that zinc acetate is precipitated by sulphuretted hydrogen. The above numbers are true only when the solution is faintly acid. Cadmium, for instance, is not precipitated by sulphuretted hydrogen from a solution strongly acidified with sulphuric or hydrochloric acid, whilst cadmium sulphide is decomposed by a strong acid.

A comparison of the results obtained by Favre and Silbermann and by Berthelot shows that the numbers given by them agree in some cases with those of Thomsen, but differ somewhat in other cases.

Magnesium hydrate has the same heat of neutralisation as the aqueous solutions of the alkalis and alkaline earths, but as it is a solid and the others are liquids, it would seem that the heat of solution of magnesium hydrate is nothing, a conclusion which has been arrived at in other ways.

The heat of formation of the sulphydrate of zinc is 2,150 heat-

units: and this sulphydrate dissolves in sodium sulphydrate with evolution of 840 units just in the same way as the oxyhydrate dissolves in sodium hydrate. G. T. A.

Formation of Haloïd Ethers in the Gaseous State. By Berthelot (*Compt. rend.*, **88**, 52—54).—The author gives the heat of vaporisation of products obtained by the combination of the halogens and haloïd acids with certain olefines.

Ethylene Dibromide.—The heat of vaporisation for 188 grams, is 8·23, whilst the heat disengaged during its formation (1) with liquid bromine is 29·3 th. units, (2) with gaseous bromine, 27·2 th. units.

The heat of vaporisation of ethyl bromide, C_2H_5Br, is 6·72 for 109 grams.

The following are the results obtained for the compounds of amylene with the haloïd acids:—

	Sp. heat.	Mol. heat.	Heat of vaporisation.
$C_5H_{10}.HCl$..	0·40 between 10° and 86°	42·6	6·0 for 106·5 gr.
$C_5H_{10}.HBr$..	0·287 „ 12° and 87°	43·3	7·30 „ 151
$C_5H_{10}.HI$..	0·219 „ 11° and 97°	43·4	9·4

The heat of vaporisation of $C_5H_{10}.HI$ is too high, owing to dissociation taking place during distillation.

From the heat of combination of these bodies (*Ann. Chem. Phys.* [5], **11**, 295), it is seen that that of $C_5H_{10}.HBr + 13·2$ is the mean of those of $C_5H_{10}.HCl$ 16·9 and $C_5H_{10}.HI$ 10·6. The heat of combination of ethylene dibromide, 27·2, is nearly double that of amyl bromide, 13·2, showing how the compounds of the olefines with the halogens and the haloïd acids are related by their heat of combination, according to the weight of bromine they contain, as well as by their chemical properties and functions. L. T. O'S.

Inorganic Chemistry.

Ozone and the Silent Electric Discharge. By Berthelot (*Compt. rend.*, **88**, 50—52).—The author finds that no combination takes place between hydrogen and oxygen when exposed to the silent discharge for several hours, in the proportion of 2 vols. of the former to 1 of the latter, although ozone is formed in considerable quantity; the tension was equal to that of a current which will give a spark 8 cm. long in air. It is remarkable that hydrogen should not combine with oxygen under the very conditions in which oxygen combines with the metals, sulphur dioxide, arsenious acid, iodine, and even nitrogen. Aqueous vapour, moreover, is not decomposed by the silent discharge, neither does it combine with oxygen to form hydrogen dioxide.

In the case of carbonic oxide, when mixed with oxygen in the proportion of 2 to 1, and exposed to the silent discharge over mercury,

the author observed the formation of a brown sub-oxide of carbon, C_2O_3; also that part of the oxygen combined with the mercury, and a portion of the carbon monoxide remained unchanged. Similar results were obtained when the oxygen was in excess. The presence of excess of oxygen does not prevent the decomposition of carbonic anhydride by the silent discharge, but the oxygen, after the reaction, contains a large amount of ozone.

By the action of the silent discharge on carbonic anhydride in sealed tubes, 16 per cent. of the gas was decomposed with the formation of a gas acting as a strong oxidising agent. If this gas be regarded as ozone, then it is produced in the proportion of from 30 to 40 per cent. of the amount of oxygen set free, which is larger than the quantity of ozone formed from pure oxygen. All attempts to isolate the gas have failed, owing to its strong oxidising properties, and the author is inclined to believe that percarbonic acid is formed.

L. T. O'S.

Liquefaction of Silicium Hydride. By Ogier (*Compt. rend.*, **88**, 236).—Silicium hydride at the ordinary temperature resists a pressure of 200 to 300 atmospheres. At $-11°$, however, it is liquefied by a pressure of 50 atmospheres; at $-5°$, under 70 atmospheres; and at $-1°$, under 100 atmospheres; but at 0° it remains gaseous under a pressure of 150 to 200 atmospheres; its critical point, therefore, is situated about 0°.

L. T. O'S.

Relative Affinity of Oxygen for Carbonic Oxide and Hydrogen. Part II. By A. Horstmann (*Deut. Chem. Ges. Ber.*, **12**, 64—69).—The author has continued his experiments on the relative affinity of oxygen for hydrogen and carbon monoxide, and has arrived at the following conclusions:—

I. The addition of carbonic anhydride to a mixture of hydrogen and carbonic oxide with insufficient oxygen for complete combustion, diminishes the amount of carbonic oxide, and increases the quantity of hydrogen burnt. Under suitable conditions, it is not only possible for the carbonic oxide to completely escape combustion, but also for a portion of the carbonic anhydride to be reduced.

II. Carbonic oxide is always formed, on exploding a mixture of carbonic anhydride, hydrogen, and oxygen.

III. In a mixture of carbonic oxide and hydrogen, the coefficient of affinity of the former does not depend on the proportion in which the two gases are present, but it varies with the relative amount of oxygen with which they are exploded. This is seen in the following table, in which the amount of oxygen is measured by the volume of gases burnt (expressed in percentages in Column I):—

I. Volume of H + CO consumed.	II. Coefficient of affinity.	I. Volume of H + CO consumed.	II. Coefficient of affinity.
15	2·68	40	6·35
20	3·80	50	5·88
25	4·83	60	5·38
30	5·65	70	4·85

The addition of carbonic anhydride to the mixture has the same effect on the coefficient of affinity as diminishing the amount of oxygen. This is probably due to the fact that carbonic anhydride lowers the temperature of combustion, thereby increasing the amount of hydrogen consumed.

IV. The ratio between the aqueous vapour and carbonic anhydride formed is equal to the ratio between the hydrogen and the carbonic oxide multiplied by the coefficient of affinity.

V. At low temperatures oxygen has a greater affinity for carbonic oxide than for hydrogen. W. C. W.

Crystalline Barium Chromate. By L. Bourgeois (*Compt. rend.*, **88**, 382—383).—On heating two equivalents of barium chloride with one equivalent of potassium chromate and one equivalent of sodium chromate to a bright-red heat, and allowing the mixture to cool, green crystals form in the interior of the fused mass. These may be isolated by boiling with water, whereby the chlorides are dissolved. They have the sp. gr. 4·6, dissolve easily in hydrochloric and nitric acid, and are decomposed by sulphuric acid into barium sulphate and chromic acid; potash also decomposes the salt. Analyses show that the crystals consist of neutral barium chromate, $BaCrO_4$, and they appear to be right rhombic prisms, isomorphous with barium sulphate. By a similar method, strontium chromate has been obtained in rhomboidal plates.

The author is continuing the research with regard to other metallic chromates. L. T. O'S.

Action of Sulphuretted Hydrogen on Alkaline Solutions of Alumina. By G. Lösekann (*Deut. Chem. Ges. Ber.*, **12**, 56—57).—Sulphuretted hydrogen precipitates hydrate of alumina from an alkaline solution; the precipitate is dissolved either on boiling the mixture, or on the addition of caustic soda. Chromium sesquioxide resembles alumina in its behaviour with sulphuretted hydrogen; the precipitate is not, however, dissolved by boiling. W. C. W.

Silver Ultramarine. By K. Heumann (*Deut. Chem. Ges. Ber.* **12**, 60—64).—In the decomposition of silver ultramarine by dilute nitric acid, one-third of the silver separates out as sulphide, the remaining two-thirds form silver nitrate. Similarly only two-thirds of the silver in the ultramarine are replaced by sodium, by long-continued boiling with a solution of sodium chloride. W. C. W.

Gases in Iron and Steel. By F. C. G. Müller (*Deut. Chem. Ges. Ber.*, **12**, 93—95).—In order to collect the gases contained in iron and steel, an ingot of the metal, standing upright in a basin of water, is pierced from below by means of a powerful drill. The gases which collect in the cylindrical bore are transferred to a eudiometer and analysed. The composition of the gases is seen from the following table:—

	I.	II.	III.	IV.
H	88·8	77·0	67·8	83·3
N	10·5	22·9	30·8	14·2
CO	0·7	—	2·2	2·5
Volume of gas, volume of metal = 100	60	45	25	35

I, Bessemer steel before the addition of spiegel iron; II, Bessemer steel after the addition of spiegel; III, Martin steel; and IV, cast iron. W. C. W.

Cobalt-ammonium Compounds. By G. Vortmann (*Deut. Chem. Ges. Ber.*, **11**, 2181—2182).—In solutions of luteo-cobalt salts, sodium pyrophosphate produces a precipitate consisting of reddish-yellow leaflets, insoluble in water and ammonia. To this compound Braun (*Annalen*, **125**, 153) assigns the formula $3(12NH_3.Co_2O_3) + 5P_2O_5 + 40H_2O$, whilst Gibbs (*Proc. Am. Acad.*, **11**, 29) attributes to it the composition $Co_2(NH_3)_{12}P_4O_{13}(OH)_2 + 5H_2O$. According to the author, a compound, $Co_2(NH_3)_{12}P_4O_{13}(ONa)_2$, is first formed, which, on washing with hot water, loses soda and takes up water. A compound containing less soda also appears to be formed. Potassium pyrophosphate produces a yellow oil, which solidifies on standing; this consists of a cobalt salt containing potassium. Potassium pyroantimonate yields a crystalline precipitate, which contains potassium. P. P. B.

Ammoniacal Mercury Compounds. By H. Gerresheim (*Liebig's Annalen*, **195**, 373—386).—The base which Millon obtained by treating mercuric oxide with aqueous ammonia has, according to the author, the composition $Hg_4O_3N_2H_4 + 2H_2O$. It is not decomposed by a boiling solution of potash; but if the mixture is evaporated to dryness, an explosion ensues. When heated at 100° in a current of dry air, it splits up into water, ammonia, mercuric oxide, and mercuric nitride. The base is insoluble in water, alcohol, and ether; it dissolves in an excess of acetic acid, and on the addition of hydrochloric, sulphuric, and nitric acid to this solution, the corresponding salt of the base is precipitated. It possesses the remarkable property of depriving all soluble salts and many insoluble salts of their acids; *e.g.*, on shaking up the base with impure caustic soda solution, the sulphates, chlorides, and other impurities are removed from the liquid.

The author suggests that small quantities of ammonia may be estimated by precipitation with mercuric chloride and sodium carbonate. The ammonia in the precipitate can be determined (1) by distilling the precipitate with sodium sulphide and hydrate, and titrating the ammonia in the distillate; (2) by dissolving the precipitate in hydrochloric acid, and precipitating with platinum chloride; or (3) by weighing the precipitate dried at 100°, which has the composition $Hg_5N_2O_2H_2Cl_2$. W. C. W.

Spitting of Silver. By T. Fluegger (*Chem. Centr.*, 1879, 30).—If silver be melted with one-tenth of its weight of borax, and, after being maintained for half an hour in a molten state, be allowed to

cool slowly, bubbles of oxygen make their escape and inflate the soft borax glass on the surface of the metal. This experiment shows that the spitting of silver is not due to pressure exerted on the inner and softer portion of the metal by contraction of the outer crust.

M. M. P. M.

Mineralogical Chemistry.

"Etch-figures" on Quartz Crystals. By H. Baumhauer (*Jahrb. f. Min.*, 1878, 655—656).—The author obtained a modification on half of the edges of +R −R on quartz-crystals by the etching action of fused caustic potash; the new faces being probably those of the trapezohedron, $\frac{P\frac{7}{5}}{4}$. In the same way he obtained a modification of the alternate prismatic edges of ∞R, the modifying form being probably the prism $\frac{\infty P\frac{4}{3}}{4}$. The form and position of the "etched-figures" upon ±R showed that the latter faces might be considered as "limitation-forms" (grenz-formen) of partially positive and partially negative trapezohedrons. The crystals examined by the author exhibited no trace of a dextrorotatory or lævorotatory individual upon the rhombohedral faces, although the presence of such individuals was indicated by the position of the "etch-figures." On examining the faces of ∞R (after being etched) under the microscope, it was found that they were divided by a twin-line into two parts, partially parallel to ∞R and partially parallel to ∞R : R; the "etch-figures" occurring in an unequal and dissimilar manner on the faces of the different individuals. From this the author concludes that the crystals under examination did not consist of two dextrorotatory or two lævorotatory individuals, as might have been inferred from the ordinary examination, but rather of portions of both varieties in combination.

C. A. B.

The "Etch-figures" Produced on the Alums. By F. Klocke (*Jahrb. f. Min.*, 1878, 654).—The figures produced by etching the octohedral faces of the alums are triangular pyramidal indentations, the angles of which are turned towards the octohedral edges. There is no distinct relationship between the size of the etched-figure and the area of the face upon which the figure is produced, and the distribution of the etched figures is also irregular; those on the cubical faces are four-sided pyramidal indentations. The rhombic dodecahedral faces do not allow of the formation of distinct "etch-figures," as those which do form are almost immediately re-dissolved. The formation of these figures is always a proof of the solution of the alum in the solvent, whilst the non-formation of the figures is not an absolute proof that the alums have not been acted upon by the solvent. The author used the method of measurement adopted by G. Rose in the case of the diamond, and obtained the following results, viz. (1). The "etch-figures" exerted no effect upon the size of the angles of the

combination-edges. (2.) The "etch-figures" produced upon the octohedral faces are those of a triakis-octohedron, whose "habit" most nearly approaches that of an octohedron. The "etch-figures" produced on the cubical faces are those of trapezohedrons, which hitherto have not yet been observed to occur in combination upon alum crystals. (3.) Different "etch-figures" are produced by acids upon the octohedral faces from those produced by the action of water upon those faces; those produced by hydrochloric and nitric acids are six-sided pyramidal depressions, but concentrated acids exert no action.

C. A. B.

Sulphide of Iron and Silver, from Andreasberg. By A. Streng (*Jahrb. f. Min.*, 1878, 630).—This mineral occurs in "penetration trillings," the individuals exhibiting the combination $\infty\breve{P}\infty . \infty\breve{P}3.2\breve{P}\infty$, with a hexagonal type. The chemical composition of this mineral is represented by the formula $Ag_2S + Fe_4S_5$. The author states that the results of the analyses of all these minerals, similar in composition to argentopyrites (silberkies), lead to the general formula $Ag_2S + pFe_nS_n + 1$, that is, a mixture of 1 molecule of Ag_2S with p molecules of a sulphide of iron having the same formula as pyrrhotite. Streng is of opinion that argentopyrites may prove to be an isomorphous mixture of Ag_2S with pyrrhotite.

C. A. B.

Cinnabar Crystals from California. By E. Bertrand (*Jahrb. f. Min.*, 1878, 657).—The crystals in question came from the Redington Mine, Lake County. They were acicular (like chalcotrichite), exhibited the combination $\infty R.\frac{4}{5}R$, and were accompanied by quartz and metacinnabarite.

C. A. B.

Double Selenides of Lead and Copper. By F. Pisani (*Compt. rend.*, **88**, 391—392).—A double selenide of lead and copper occurs in the Cordilleras, South America, associated with other selenides, also azurite, malachite, and chrysocolla. Sometimes it is found disseminated, and at other times in small masses of micro-crystalline structure. It is generally of a leaden-grey colour, but occasionally its colour resembles that of phillipsite. The sp. gr. of different varieties of the grey mineral varies from 5·5 to 7·55. The best method for analysing it consists in decomposing the mineral with chlorine; when nitric acid is used for this purpose, some selenite of lead comes down on separating the lead by sulphuric acid; moreover, selenium precipitated by sulphurous anhydride always contains some copper; sometimes selenium is found with the copper. The analyses of the grey variety, which differ considerably, correspond with the formula of zorgite (Pb.Cu)Se, whilst the other variety, which has the sp. gr. 6·26, may be represented by the formula $(PbCu)_3Se_2$.

L. T. O'S.

Dietrichite, a New Alum, from Hungary. By v. Schroeckinger (*Jahrb. f. Min.*, 1878, 652).—This mineral occurs in fibrous, sheaf-like groups, H. = 2·1. Dirty-white to brownish-yellow colour. Silky lustre. Acid taste. Easily soluble in water. Fusible before the blowpipe. Chemical composition as follows, viz.:—

ZnO.	FeO.	MnO.	MgO.	Al_2O_3.	SO_3.	H_2O.
3·70	3·11	1·74	0·33	10·92	35·94	44·48 = 100·32

The formula corresponding with this composition is $ZnSO_4 + Al_2 3SO_4 + 23H_2O$, thus proving the mineral to be a somewhat dehydrated zinc-alum. It is found at Felsöbanya, where it has been formed during the last 14 years. Named in honour of the chemist Dietrich.

C. A. B.

Wagnerite from Bamle, in Norway: a Russian Retinite. By F. Pisani (*Compt. rend.*, **88**, 242—244).—*Wagnerite*, a double magnesium phosphate and fluoride, occurs crystalline in Werfen, in Salzbourg: an analogous mineral known as kjerulfine, containing several per cent. of lime, occurs in yellow masses at Bamle, in Norway. It is sometimes obtained crystallised in large rhombic prisms, which are for the most part homogeneous, being formed of a yellow vitreous substance, wagnerite; but here and there white veins of apatite appear, in the midst of which crystals of wagnerite occur. Again crystals of wagnerite are found, entirely coated with a crust of white stony apatite; it is therefore apparent that apatite and wagnerite are pseudomorphous. The analysis of wagnerite from Bamle gave the following results:—P_2O_5, 43·7; MgO, 34·7; CaO, 3·1; Mg, 6·8; Fl, 10·7; residue, 0·9, which corresponds with the formula $(MgOCaO)_3P_2O_5.MgF_2$; it has the sp. gr. 3·12. It appears, therefore, that kjerulfine and wagnerite are the same mineral; the large quantity of lime in the latter, which sometimes amounts to 10 per cent., shows its great tendency to change with apatite.

Russian retinite, or Russian magnesium garnet, is a massive mineral, easily fusible, and possessing the colour of garnet. On heating, it swells up and turns white before melting. Its density is 2·31, and its analysis, which shows it is not a garnet, is as follows:—SiO_2, 67·5; Al_2O_3, 16·34; Fe_2O_3, 1·16; K_2O, 3·88; Na_2O, 3·92; CaO, 2·20; loss on ignition, 5·90.

L. T. O'S.

Pseudobrookite and Szaboite, New Minerals. By A. Koch (*Jahrb. f. Min.*, 1878, 652).—These minerals occur as sublimation-products in small crystals in a decomposed augite-andesite, at the Aranyer Berg, Siebenburgen, accompanied by hornblende and tridymite. *Pseudobrookite*, rhombic, in tabular crystals, exhibiting the forms $\infty P\bar{\infty}$. ∞P. $\infty P\breve{\infty}$. $P\bar{\infty}$. $\frac{1}{3}P\bar{\infty}$. The macropinacoid is striated vertically; cleavage brachydiagonal; uneven fracture; H. = 6; sp. gr. = 4·98; dark brown to iron black; streak ochre-yellow; opaque to translucent, in very thin splinters, metallic adamantine lustre; infusible before the blowpipe, but soluble in concentrated sulphuric acid. Chemical composition as follows, viz.:—

TiO_2.	Fe_2O_3.	CaOMgO.	Loss on ignition.
52·74	42·29	4·28	0·70 = 100·01.

From the above analysis it is evident that the mineral is titanic iron and dimorphous with ilmenite. It was named pseudobrookite on account of its resemblance to brookite.

Szaboite (in honour of Professor Szabo), asymmetrical crystals, very

small and thin, 1 mm. in diameter. Forms observed $\infty P \bar{\infty}$ (strongly striated vertically), $\infty P'|. \infty P\bar{\infty} . 'P'|. {}'P \bar{\infty} {}'|.$ H. = 6; sp. gr. = 3·505; brown, with a copper-red streak; vitreous lustre on the vertical faces; opaque to translucent; weak dichroism; infusible before the blowpipe, but somewhat strongly attacked by concentrated hydrochloric acid. Chemical composition as follows, viz.:—

SiO_2.	Fe_2O_3.	CaO.	Loss on ignition.	
52·35	44·70	3·12	0·40	= 100·57.

C. A. B.

The Crystal-form and Twin-formation of Leucophane. By E. Bertrand (*Jahrb. f. Min.*, 1878, 656—657).—An optical examination of thin plates of this mineral, cut parallel with the most distinct cleavage direction, showed that there were two systems of rings, belonging of course to two distinct crystals, which were twinned. The outward form of the crystals appeared to be monosymmetrical or rhombic. Bertrand sent his preparations to Groth, who examined them, and found the crystal system to be monosymmetrical. The crystals are quadralings, and exhibited the following forms in combination, viz.:— ∞P. OP. + P. $\infty \breve{P} \infty$. $2\breve{P}2$. $\frac{1}{2}\breve{P}\infty$.; twin plane a face of $+ \breve{P}\infty$; axial ratio $a : b : c = 1·061 : 1 : 1·054$; cleavage, clinodiagonal. Leucophane occurs on coarse-grained felspathic veins, accompanied by ägerine, eläolite, magnetite, and mosandrite on the Island of Loven, Langesundfjord, Norway. C. A. B.

Diopside. By C. Doelter (*Jahrb. f. Min.*, 1878, 657).—The author has analysed numerous specimens of diopside, and states that it is incorrect to consider as impurities the ferric oxide and alumina present, as the amounts of those substances actually found by analysis bear no relation to the quantity of enclosed impurity in diopside observed under the microscope. The author believes that the alumina and ferric oxide exist as silicates. C. A. B.

Bravaisite, a New Mineral. By E. Mallard (*Jahrb. f. Min.*, 1878, 653).—A small layer of this mineral occurs in the coal-formation at Noyant (Allier Department), with coal and bituminous schists; it resembles a slatey clay; hardness (when dry), = 1 to 2; sp. gr., 2·6; grey to greenish colour. Examined microscopically, the mass is found to consist of fine, crystalline, doubly-refracting fibres, arranged parallel with each other. The optical properties appear to warrant the conclusion that the crystals are rhombic; easily fusible before the blowpipe to a white bead, and attacked by acids. Chemical composition as follows, viz.:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	H_2O.
51·40	18·90	4·00	2·00	3·30	6·50	13·30 = 99·40.

Deducting the ferric oxide, which is derived from iron-pyrites present as an impurity, the formula, $4·5SiO_2.Al_2O_3RO + 4H_2O$, is obtained; this places the mineral amongst the zeolites. Named in honour of the chemist Bravais. C. A. B.

Diabase from Berneck. By W. Knop (*Chem. Centr.*, 1879, 41—44).—At Berneck in the Fichtelgebirge a green diabase occurs, portions of which have been much weathered. The author has analysed the rock, and also the soil produced from it by the action of the weather. His results are contained in the following table:—

	Diabase.			Soil.	
	I.	II.	III.	Finer parts.	Coarser parts.
Water	5·70	5·70	5·50	14·297	11·56
Humus	—	—	—	1·580	0·50
Loss on ignition	5·70	5·70	5·50	15·877	12·06
	Ignited residue.				
Carbonic acid	1·06	1·04	1·07	trace	trace
Lime	12·25	—	10·70	8·739	14·50
	8·24	7·50	6·08	8·027	
Potash	1·09	—	—	0·801	—
Soda	0·70	—	—		
Iron oxide	38·94	38·45	—	19·140	37·60
Alumina				15·859	
Silicic acid	38·49	38·10	—	47·434	47·90
	100·77			100·000	100·00
SiO_2 + silicates	100·00			100·00	
Aluminium silicate	50·00			57·827	62·4
Other Bases	50·00			42·173	37·6

M. M. P. M.

The Gneiss of the North Eastern Schwartzwald and its Relationship to the Mineral Veins. By K. Killing (*Jahrb. f. Min.*, 1878, 657—658).—The author examined numerous varieties of gneiss from the above locality, and came to the conclusion that the highly micaceous gneiss of the Schapbachthal furnished the material for the mineral veins. He found in this rock the following percentage amounts of metallic constituents, viz., Fl, 0·28; PbO, 0·28; CuO, 0·700; Bi_2O_3, 0·0056; CoO, 0·0094. Several tables are given by Killing showing the percentage differences between fresh and weathered gneiss. The fresh gneiss contains chlorides and sulphates (in the fluid enclosures of the quartz), and the *mica* contains cobalt, copper, lead, and bismuth, the percentage amounts being given in the above-mentioned tables, whilst it has long been known that felspar contains a certain amount of barium, so that the origin of the minerals present in the veins of the locality in question is almost beyond dispute. The author calculated how much of the original rock would be required to furnish a certain amount of mineral ore, obtaining the following results, viz., 1 cubic metre (2,720 kilograms) of the fresh, granular, streaked gneiss would furnish (in grams):—

Galena.	Copper-pyrites.	Barytes.	Fluorspar.
92·48	388·96	10608·00	1332·80

1 cubic metre (2,760 kilograms) of the fresh slatey gneiss would furnish (in grams) :—

Galena.	Copper-pyrites.	Barytes.	Fluorspar.
133·17	564·62	9384·00	1959·60

C. A. B.

The Existence of Barium and Strontium in all Rocks Constituting the Primary Formation, and the Origin and Mode of Formation of their Compounds in their present Places of Occurrence. By L. Dieulafait (*Ann. Chim. Phys.* [5], **15**, 530—563).—The object of the author in this paper has been to show that barium and strontium exist in all the so-called primary rocks, such as the different varieties of granite, gneiss, and syenite, and to trace their passage from these to their present places of occurrence. The main portion of the paper is occupied by a clear account of his work in the laboratory and in the field, which has led him to form the following conclusions :—

(1.) All primary rocks contain barium and strontium in sufficient quantity to be easily determined in 1 gram of the following minerals : felspars (orthose, oligoclase, albite), mica, either in the primary rocks or in their transformations, gneiss, true small-grained granite, true large-grained granite, and syenite.

(2.) Barium and strontium have been extracted from primary rocks by the action of water aided by a sulphurising body, of which the existence is more particularly indicated by the fact that barium sulphate is almost always associated with sulphides (galena, blende, pyrites).

(3.) As the waters which acted on the primary rocks seem generally to have been in motion, and on the other hand the formation of the carbonates and sulphates from the sulphides of barium and strontium are necessarily successive, these two orders of compounds have rarely been deposited in the same place. This explains in the most natural manner the fact that the different compounds of both substances are rarely if ever found in the same deposit.

(4.) Owing to their difference in solubility, larger quantities of strontium than of barium have been taken up by sea-water.

(5.) The sulphates thus dissolved were deposited together with the gypsums on spontaneous evaporation, but as the gypsums of all ages contain large quantities of ammoniacal salts and organic matter, the sulphates of lime, barium, and strontium, are transformed into sulphides by the action of these substances, as pointed out by Chevreul long ago. Those of barium and strontium being much more soluble were separated out, and by the action of the carbonic anhydride and oxygen of the air again transformed into carbonates and sulphates, which were again deposited, the strontium sulphate being frequently accompanied by crystals of free sulphur.

According to the author, the following is the mode of formation of the carbonate and sulphates of strontium often found along with deposits of common salt. The deposits of strontium found at the

present day differ entirely from those of barium; this difference is caused by the strontium found associated with rock salt being in its second stage of evolution, whilst barium, mainly on account of its greater insolubility, remains in the first stage; but he considers that both barium and strontium, whenever they occur, must be derived from one or other of the primitive rocks.

(6.) From the above the author draws the following important inference. If barytes (barium sulphate) did not originate in the lodes or veins in which it is now found, but, as he believes, has been extracted, molecule by molecule, from the primary rocks, it naturally follows that the metalliferous minerals of which barytes forms the gangue or with which it is simply associated, must have the same origin. These minerals are very numerous, the most important being those of manganese, lead, and zinc. To prove this, the author considers that it will be necessary to demonstrate the two following propositions:—1. Can all minerals associated with barium salts be traced back to the primary rocks? 2. Do the primary rocks contain appreciable quantities of the metals whose minerals are found associated with barium sulphate and carbonate?

(7.) The author considers that the first proposition has been satisfactorily answered in the affirmative, as far as the metals treated of in this paper (Mn, Pb, Zn) are concerned, and that the second proposition has been so also, as far as the only metal (Mn) which he has as yet investigated is concerned. He concludes by stating that he hopes shortly to prove it for lead, zinc, and several other metals.

J. M. T.

On Cleopatra's Needle. By G. W. Wigner (*Analyst*, 1878, 382—384).—The sp. gr. of fragments taken from different parts of the obelisk was remarkably constant at 2·682. The absorbent power of the unchanged stone was at the rate of about 7·8 grains of water per square foot; the weathered surface showed an absorbent power six times as great. After powdering the stone and separating the constituent minerals by means of Sonstadt's solution, there were found of mica 9 per cent., of quartz 22, and of felspar 69. The sp. gr. of these minerals were: mica, 2·986; quartz, 2·747; felspar, 2·595. The proportion of mica varied considerably in different parts of the stone. The stone contained SiO_2, 68·18; Fe_2O_3, 4·10; Al_2O_3, 16·20; CaO, 1·75; MgO, 0·48; Na_2O, 2·88; K_2O, 6·48; and a trace of Mn. In the weathered portion the Al_2O_3 was decreased to 15·37, the Na_2O to 2·40, and K_2O to 5·34, whilst the lime was increased to 2·05. The felspar contained SiO_2, 63·88; Fe_2O_3 and Al_2O_3, 22·25; CaO, 1·09; MgO, 0·45; Na_2O, 1·84; K_2O, 10·66; and a single analysis of the mica yielded SiO_2, 46·16; Fe_2O_3, 7·30; Al_2O_3, 41·18; MgO, 6·77; Na_2O, 0·92; K_2O, 5·24. F. C.

Examination of a Meteorite found in the Neighbourhood of Berdjansk. By M. Hiriakoff (*Jahrb. f. Min.*, 1878, 653—654).—The meteorite in question weighed 22·56 grams, and had a sp. gr. of 6·53. From the results of a chemical and microscopical examination, the author concludes that it must be classed with the Pallas meteorites, or else be ranged immediately next to them, as it consists of a nickeliferous iron, with 0·66 per cent. of olivine and triolite disseminated

throughout the mass. The meteorite dissolves completely in hydrochloric acid with an evolution of sulphuretted hydrogen, and on evaporating down the solution, a considerable residue of silica remains. No "Wiedmannstätten figures" were obtained on etching a ground surface of the meteorite, but a peculiar spongy structure was exhibited in consequence of the decomposition of the embedded grains of olivine. C. A. B.

Mineral Waters of Auvergne. By E. Willm (*Bull. Soc. Chim.* [2], **31**, 3—9).—The paper describes the mode of analysis adopted in the examination of the waters of thirteen springs situated at Royat, Saint-Nectaire, and Châtel-Guyon, in Auvergne, and presents the results in tables, from which those given below are selected as types of the waters of each locality:—

Locality	Royat.	Saint-Nectaire.	Châtel-Guyon.
Name of the Spring	Eugénie.	Saint-Cézaire.	Deval.
	grams.	grams.	grams.
Total carbonic acid	3·2242	2·9810	2·9152
Free „ „	1·3955	0·5192	1·8442
Combined carbonic acid (bicarbonates)	1·8287	2·4618	1·0710
Silica	0·1026	0·1355	0·1110
Alumina	—	—	traces
Iron	0·0259	0·0055	0·0147
Calcium	0·3106	0·1853	0·6820
Magnesium	0·0999	0·0859	0·3988
CO_3 (in deposit by boiling)	0·7426	0·4928	—
CO_3 (combined with alkalis)	0·5050	1·1857	1·2573
Chlorine	1·0151	1·6854	2·1558
Sulphuric acid, SO_4	0·1102	0·1170	0·3559
Sodium	1·0222	1·9177	0·9042
Potassium	0·0808	0·1978	0·0991
Lithium	0·0061	0·0095	0·0024
Arsenic	0·0003	0·0009	0·0006
Iodine (traces in some of the springs)	—	—	—
Total contents per litre	4·0216	6·0190	5·9818

R. R.

Organic Chemistry.

Action of Hypochlorous Acid on Ethylene. By L. Pebal (*Deut. Chem. Ges. Ber.*, **11**, 2188—2189).—E. Fürst has observed that when these two compounds act on one another in sunlight, an oily liquid is obtained which crystallises after standing for some time over sulphuric acid. The aqueous solution of these crystals when neu-

tralised with calcium carbonate yields calcium glycolate. This and the analytical results show that the product of the action of hypochlorous acid on ethylene is monochloracetic acid. P. P. B.

Hydrocarbons from American Petroleum. By L. Prunier (*Compt. rend.*, **88**, 316—387).—In a previous note (*Compt. rend.*, December, 1878, and this volume, p. 309), the author called attention to certain hydrocarbons very rich in carbon, obtained by the redistillation of American petroleum. By the action of certain solvents, the author has isolated a granular crystalline substance, soluble in carbon bisulphide and in hot chloroform. On evaporating the latter, a reddish-brown residue was obtained, which gave results corresponding with the formula $(C_6H_2)_n$. It is, however, a mixture from which different bodies, equally rich in carbon, may be obtained, forming a new series of hydrocarbons. By treatment with alcohol containing a few per cent. of chloroform, a yellowish body, with a pearly lustre, is obtained. It crystallises in very slender needles, and forms compounds with picric acid. It melts at 260°, is electric, and shows an intense blue fluorescence. It is nearly insoluble in alcohol, ether, and warm chloroform, but is soluble in petroleum, benzene, and acetic acid. The analyses correspond with the formula $(C_6H_2)_n$. The picrates, of which two are formed, have the formulæ $C_{24}H_8.C_6H_3(NO_2)_3O$, melting at 185°, and $C_{24}H_8.2C_6H_3(NO_2)_3O$, melting at 135°. L. T. O'S.

Eikosylene, a Derivative of Lignite Paraffin. By E. Lippmann and J. Hawliczek (*Deut. Chem. Ges. Ber.*, **12**, 69—73).—The mixture of chlorides which is formed by the action of phosphorus pentachloride on lignite paraffin (m. p. 37°) is decomposed on distillation, even *in vacuo*. That portion of the liquid which boils between 225° and 230° has the composition $C_{20}H_{39}Cl$. When distilled under the ordinary atmospheric pressure, it splits up into hydrochloric acid, and a new hydrocarbon, $C_{20}H_{38}$, b. p. 314—315°, which the authors call *eikosylene*. This body combines with 2 atoms of chlorine and bromine to form oily liquids. Eikosylene can also be obtained from the products of the action of phosphorus pentachloride on ozokerit (m. p. 63°). W. C. W.

Action of Dilute Sulphuric Acid on Allyldimethylcarbinol. By A. Saytzeff (*Bull. Soc. Chim.* [2], **31**, 72).—In studying the alcohols of the series $C_nH_{2n-3}.OH$, synthetically obtained, the author found that the action of dilute sulphuric acid on allyldimethylcarbinol gave rise to a hydrocarbon C_6H_{10}, as well as its polymeride, $C_{12}H_{20}$, whilst allyldipropylcarbinol, under the same conditions, yielded the hydrocarbon $C_{10}H_{18}$. The author considers that the formation of $C_{12}H_{20}$ is analogous to that of isodibutylene, to which he conceives its constitution is analogous, and thus represents it:—

$$Me_2C:C(CH:CH_2).CMe_2.CH_2.CH:CH_2.$$

The structural resemblance of this formula to that which probably belongs to the terpenes, leads the author to believe that the hydrocarbon $C_{12}H_{20}$ is nearly allied to them. R. R.

Allyldiethylcarbinol. By SCHIROKOFF and A. SAYTZEFF (*Bull. Soc. Chim.* [2], **31**, 67).—The diethylacetone used by the author in his synthesis of allyldiethylcarbinol, was obtained by the dry distillation of the calcium salt of propionic acid, prepared synthetically from ethyl cyanide. The diethylacetone and allyl iodide were employed in the proportion represented by the equation $(C_2H_5)_2CO + C_3H_5.Zn.I = (C_3H_5)(C_2H_5)_2C.OZnI$. The product of this reaction was treated as in the case of allyldimethyl carbinol. Allyldiethylcarbinol is a colourless liquid (b. p. 156°) with a peculiar odour, like that of camphor. It unites readily with bromine, forming a compound analogous to those obtained with allyldimethyl carbinol and allyldipropylcarbinol. The oxidation of allyldiethyl carbinol by potassium dichromate and sulphuric acid yields diethylacetone, and acetic and propionic acids.

R. R.

Influence of Metallic Chlorides on Etherification. By BERTHELOT (*Ann. Chim. Phys.* [5], **15**, 238—240).—Experiments were made with the object of discovering if the union of alcohol with acids (particularly acetic acid) was modified by the presence of metallic chlorides, either as to time required or limit. 100 parts of commercial absolute alcohol was mixed with $62\frac{1}{2}$ parts of glacial acetic acid, and the mixture placed in a flask with 5 grams of a metallic chloride. The chlorides of sodium and potassium were very finely powdered, those of barium, zinc, aluminium, were introduced in large pieces; also the following chlorides with crystalline water were experimented with: barium, strontium, and calcium chloride, but of each of these 10 grams were taken. The flasks were frequently shaken, and from time to time the amount of acid in the solution was estimated on a small sample of the liquid, by means of baryta-water. In the case of the zinc and aluminium chlorides, the acidity of these was determined to begin with in the alcoholic solution, before the addition of the

	Weight of acid converted into acetic ether.					
	At moment of mixture.	After 6 hours.	After 24 hours.	After 8 days.	After 1 month.	After 2 months.
NaCl	0	—	2·0	13·7	32·2	47·3
KCl	0	—	2·3	15·1	33·3	46·4
KBr	0	0·5	3·5	19·0	37·9	52·2
KI	0	—	3·5	23·9	Iodine set free. Titration impossible.	—
$BaCl_2$	0	1·7	4·6	19·3	38·8	52·4
$BaCl_2 + 2H_2O$	0	—	6·6	20·6	35·9	53·7
$SrCl_2$	0	6·8	19·0	43·5	54·2	70·6
$SrCl_2 + 6H_2O$	0	4·5	13·4	39·5	58·1	69·5
$CaCl_2$	0	4·2	10·2	33·2	55·3	64·7
$CaCl_2 + 6H_2O$	0	6·3	20·5	49·7	69·4	77·6
$MgCl_2$	0	11·3	22·7	38·0	53·8	63·6
$ZnCl_2$	0	0·8	4·2	26·5	51·2	—
$CuCl_2$	0	5·3	16·9	54·8	77·0	77·0
Al_2Cl_6	0	48·3	64·5	74·2	73·3	—

acetic acid, and the number obtained afterwards deducted. It is accurate enough for comparative results. The table gives the results calculated on 100 parts of original acetic acid. The relative limit of the mixture, without the chloride, $2C_2H_5.OH + CH_3.COOH$, is 85·8.

Thus it is observed that the presence of the above chlorides in small quantity accelerates the etherification, the acceleration being more marked when the more easily decomposable chlorides are used. In point of stability, barium chloride resembles the alkaline chlorides, whilst calcium and strontium chlorides approach magnesium and cupric chlorides. W. S.

Action of Hydrocyanic Acid on Epichlorhydrin. By J. v. Hörmann (*Deut. Chem. Ges. Ber.*, **12**, 23—24).—A nitrile of chloroxybutyric acid, $C_3H_5.ClO.CNH$, is obtained by heating a mixture of hydrocyanic acid with epichlorhydrin in sealed tubes, at 40—70°. On extracting the product of the reaction with ether, and evaporating the ethereal solution, the nitrile remains as a brown liquid, soluble in water and in alcohol. The acid obtained by the action of dilute sulphuric acid on the nitrile is a thick, syrupy liquid, soluble in water. All its salts are soluble in water, and are uncrystallisable.

W. C. W.

On Glycide. By Hanriot (*Compt. rend.*, **88**, 387—388).—Glycide, $O<\begin{matrix}CH.CH_2.OH\\CH_2\end{matrix}$, the first anhydride of glycerin represents the alcohol of epichlorhydrin, $O<\begin{matrix}CH_2.CH_2Cl\\CH_2\end{matrix}$. It cannot be obtained by the action of dehydrating agents, as might be expected, but is best prepared by the action of 28 grams baryta on 48 grams monochlorhydrin, dissolved in 50 grams ether; after the action has ceased, 200 grams ether are added to extract the glycide; after the distillation of the ether this remains as a colourless, odourless liquid, of sweet taste, soluble in water, alcohol, and ether, and having a sp. gr. 1·165. It boils at 157° under the ordinary pressure, and when pure can be distilled without decomposition, but if traces of glycerol (glycerin) are present it polymerises. It combines with water, forming glycerol; and with acids to form ethereal salts. By gently warming a mixture of glycide and nitric acid, diluted with ten times its weight of water, and after cooling, saturating the solution with sodium carbonate, *mononitroglycerol* is formed and may be extracted by a mixture of alcohol and ether. It is a yellow liquid, soluble in water and alcohol, and sparingly in ether. It cannot be distilled, but on heating emits white fumes, which take fire spontaneously; it does not explode by percussion.

The author has studied the action of hydrochloric and acetic acids on glycide. L. T. O'S.

Sugars. By M. Hönig and M. Rosenfeld (*Deut. Chem. Ges. Ber.*, **12**, 45—47).—Sodium levulose and lactose are obtained as yellowish-white, deliquescent powders, when sodium alcoholate is added to a solution of the sugars in 99 per cent. alcohol.

Sodium levulose, $C_6H_{11}NaO_6$, loses 1 molecule of water at 100°, whilst sodium lactose loses 2 molecules of water. W. C. W.

Analysis of Honey from Ethiopia. By A. Villiers (*Compt. rend.*, **88**, 292—293).—A sample of this, sent to France, by M. Pierre Arnoux, is said to be found in cavities underground, without wax, and is the product of an insect like a large mosquito. It is called by the natives *tazma*, and is used to cure sore throat. It contains in 100 parts—

Water	25·5
Fermentable sugar (lævulose with a sixth of glucose in excess; free from cane sugar)	32·0
Mannite	3·0
Dextrin	27·9
Ash	2·5
Unestimated and loss	9·1

The dextrin feebly reduced tartrate of copper, and gave no colour with iodine; its rotatory power for the sodium flame was about 71°, about half that of the dextrins of feeble rotatory power and without action on iodine, which have recently been studied by Bondonneaux, and by Musculus and Gruber. The honey also contained a small proportion of a bitter principle, which could be isolated. It was free from nitrogen.

The composition of this honey resembles that of the mannas of Sinai and Kurdistan, analysed by Berthelot (*Ann. Chim. Phys.* [3], **67**, 82), that of the sweet substance of lime leaves analysed by Boussingault (*ibid.*, **25**, 5), and that of common honey. It differs from these by the absence of cane sugar. J. M. H. M.

Hydrazine Compounds of the Paraffin Series. By E. Fischer (*Deut. Chem. Ges. Ber.*, **11**, 2206—2211).—Diethylhydrazine is formed from nitrosodiethylamine in the manner already described by the author (*Ber.*, **8**, 1587), viz., by the reduction of its aqueous solutions with zinc-dust and acetic acid. On supersaturating the resulting solutions with potash, and distilling, an aqueous solution of the base distils over mixed with ammonia and diethylamine. The formation of these compounds is expressed as follows:—

$$(1)\ Et_2N.NO + 2H_2 = Et_2N.NH_2 + H_2O.$$
$$(2)\ Et_2N.NO + 3H_2 = Et_2NH + NH_3 + H_2O.$$

The ammonia is removed by neutralising the distillate with hydrochloric acid, and evaporating until the ammonium chloride crystallises out; this may be easily separated from the deliquescent salts of the other bases. The salts are again converted into the bases, and these treated with ethyl iodide. By this means the diethylhydrazine is converted into triethylazonium iodide, $Et_3N_2H_2I$, and the diethylamine into triethylamine; the formation of tetraethylammonium iodide is to be avoided. The ethyl iodide is separated by adding water and extracting with ether, the aqueous solution is then treated with potash, and the volatile base removed by distillation. The azonium compound is non-volatile, and is separated from the residue by adding concentrated

caustic potash; it forms an oil, which solidifies on standing. By crystallisation from hot alcohol, in which it is easily soluble, it is obtained in colourless needles, readily soluble in hot water, but insoluble in concentrated alkaline solutions. This compound has the composition $Et_3N_2H_2I$. It forms an insoluble compound with platinic chloride, and by the action of silver oxide is converted into an alkaline hydroxide, which is easily soluble in water. This hydroxide is decomposed by heat into water, ethylene, and diethylhydrazine, affording a method of obtaining pure diethylhydrazine. It is a mobile colourless liquid, having an ammoniacal odour, is easily soluble in water, alcohol, and ether, but insoluble in concentrated alkaline solutions. It boils between 74—78°. The salts of this base are easily soluble in water and alcohol. With picric acid it forms a sparingly soluble salt, which crystallises in slender yellow needles. Its aqueous solutions are decomposed on boiling, with evolution of nitrogen. By the action of potassium cyanate, the neutral salts of this base are converted into a urea derivative, $Et_2N.NH.CO.NH_2$, easily soluble in water, from which it may be obtained by supersaturating with caustic potash and extracting with ether. It crystallises in large thin plates, and forms a double salt with platinum chloride, $[Et_2N_2H.CO.NH_2]_2PtCl_6$, which crystallises from alcohol in fine yellow needles. This urea is decomposed by boiling potash into carbonic acid, ammonia, and diethylhydrazine. Nitrous acid converts it into an oily unstable nitroso-derivative.

Diethylhydrazine is oxidised by Fehling's solution, and is resolved into diethylamine and nitrogen, as follows :—$Et_2N.NH_2 + O = 2Et_2NH + H_2O + N_2$. By more energetic oxidising agents, such as mercuric oxide, it is resolved into tetrazone, Et_4N_4. Tetrazone is a slightly yellow oil, having an odour like garlic. It solidifies at −17°, and is non-volatile. When heated to 135—140°, it is decomposed into diethylamine, nitrogen, and a liquid having an irritating odour. Tetrazone has basic properties, is dissolved by acids, and reprecipitated from these solutions by alkalis. Its platinum salt separates from its alcoholic solutions in golden-yellow needles, having the composition $(Et_4N_4)_2PtCl_6$. This salt dissolves in water, but when the aqueous solution is boiled, it is decomposed into nitrogen, diethylamine, and aldehyde. The same result takes place when it is boiled with mineral acids. The formation of diethylamine may be expressed as follows :—$Et_4N_4 + H_2 = 2Et_2NH + N_2$. This reduction takes place at the expense of one of the ethyl groups, and hence the formation of aldehyde. This behaviour of tetrethyltetrazone shows its constitution to be $Et_2N.N:N.NEt_2$, and that it is analogous to the compound $EtON:NOEt$, obtained by Zorn (*Ber.*, **11**, 1330) from nitrosyl silver and ethyl iodide. Tetrethyltetrazone precipitates the salts of the heavy metals; with mercuric chloride it forms a white crystalline precipitate, $Et_4N_4HgCl_2$. It reduces silver salts, and forms an explosive compound with iodine.

Diethylhydrazine is resolved by nitrous acid into diethylamine and nitrous oxide, thus, $Et_2N.NH_2 + HNO_2 = Et_2NH + N_2O + H_2O$.

P. P. B.

Conversion of Aldehyde into Mercaptan. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **11**, 2203—2206).—Acetaldehyde, when

treated with sulphuretted hydrogen, yields the two compounds $C_2H_4O + C_2H_4S$ and C_2H_4S. This sulphaldehyde is a liquid, and like aldehyde is easily converted into polymeric modifications (*Ber.*, **9**, 806, 1893; **10**, 1877; **11**, 1023). When this polymerisation takes place, gases are evolved, containing some sulphuretted hydrogen. Hydriodic acid (b. p. 127°) converts liquid sulphaldehyde into the solid modification; at the same time sulphuretted hydrogen is formed, and a compound which yields a white precipitate with an alcoholic solution of mercuric chloride. Solid sulphaldehyde heated in sealed tubes at 160° with hydriodic acid yields the same products of decomposition. When the liquid thus formed is treated with soda and distilled, ethyl disulphide passes over, and may be converted into mercaptan by treatment with water and zinc-dust. This change may be expressed as follows:—

$$(CH_3.CHS)_2 + H_2 = (CH_3.CH_2S)_2, (CH_3.CH_2)_2S_2 + H_2 = 2CH_3.CH_2.SH.$$

P. P. B.

Action of Aldehydes on Chloral-ammonia. By R. Schiff (*Deut. Chem. Ges. Ber.*, **11**, 2166—2167).—Chloral-ammonia and benzaldehyde react on one another, forming water and a crystalline compound. This, when recrystallised from benzene, is obtained in white leaflets, melting at 130°, and having the composition

$$C_6H_5.CH:N.CH(OH).CCl_3.$$

Valeraldehyde, furfuraldehyde, œnanthol, and acetaldehyde behave similarly with chloral ammonia.

Benzylidenchloral-ammonia is easily decomposed by dilute acids, boiling alcohol and water; when gently heated with a dilute alcoholic solution of phenylthiocarbimide, it forms benzaldehyde, chloral, and monophenylurea (m. p. 148—149°). By dry distillation it is resolved into chloral, benzaldehyde, HCl, and a resinous mass. Butylchloral-ammonia dissolved in alcohol reacts slowly on benzaldehyde, yielding trichlorobutylidenimide, which has been described by Pinner and Klein (*Ber.*, **11**, 1491). The author finds its melting point to be 169—170°, and not 163—164°. P. P. B.

Zinc Acetate. By N. Franchimont (*Deut. Chem. Ges. Ber.*, **12**, 11—13).—The author finds that zinc acetate crystallises with two molecules of water, and not three, as is generally stated. The crystals melt at 235—237°, whilst the anhydrous salt melts at 241—242° with sublimation. Under a pressure of 150 mm. zinc acetate sublimes at 200°, apparently without decomposition. W. C. W.

On Schützenberger's Chlorine and Iodine Acetates. By B. Aronheim (*Deut. Chem. Ges. Ber.*, **12**, 26—30).—The author regards the oily liquid which Schützenberger obtained by passing a current of hypochlorous anhydride into acetic anhydride, as a mixture, and not a chemical compound, since it does not act on iodine to form iodine acetate, $I(C_2H_3O_2)_3$. The author also failed to obtain the latter compound by the action of hypochlorous anhydride on iodine suspended in acetic anhydride. W. C. W.

Identity of Acetopropionic Acid and Lævulinic Acid. By M. Conrad (*Deut. Chem. Ges. Ber.*, **11**, 2177—2179).—Aceto-propionic acid is obtained by digesting ethyl aceto-succinate with dilute hydrochloric acid. After expelling the alcohol and distilling, ethyl aceto-propionate, boiling at 200—210°, and acetopropionic acid, boiling at 235—245°, were obtained. Dilute sulphuric acid decomposes ethyl acetosuccinate in the same manner. To prepare lævulinic acid, the author heats on a water-bath a mixture of 500 grams of cane-sugar dissolved in 1,000 c.c. of water, with 250 grams of concentrated hydrochloric acid. The lævulinic acid is extracted with ether; the liquid left after evaporating the ether distils between 230—250°.

The melting point of acetopropionic acid is identical with that of lævulinic acid (Tollens and Grote, *Ber.*, **10**, 1442). Both these acids boil at 239°, and their ethyl salts have identical boiling points. The sp. gr. of the two acids at 15° is 1·135. The index of refraction and the dispersive energy of these acids are also identical. Their silver salts crystallise in long tables; they have also the same solubility in water. Calcium acetopropionate crystallises from aqueous solutions in needle-shaped crystals containing 2 mols. of H_2O, agreeing therefore with the calcium lævulinate.

From the identity of these two acids, and the fact that cane-sugar, inulin, carragheen-sugar, gum, filter-paper, wood, and grape-sugar, all yield lævulinic acid, the author concludes that 5 carbon atoms in all these bodies are normally linked together. P. P. B.

Ethereal Salts of Tribasic Formic Acid. By A. Deutsch (*Deut. Chem. Ges. Ber.*, **12**, 115—119).—The ethers of tribasic formic acid are best prepared by the action of sodium on a mixture of chloroform, and the alcohol diluted with ether. The boiling points and specific gravities of these bodies are given in the following table:—

	Boiling point.	Sp. gr. at 23°.
Methyl salt, $CH(OCH_3)_3$..	101—102°	0·974
Ethyl ,, $CH(OC_2H_5)_3$..	145—147°	—
Propyl ,, $CH(OC_3H_7)_3$..	196—198°	0·879
Isobutyl ,, $CH(OC_4H_9)_3$..	220—222°	0·861
Isoamyl ,, $CH(OC_5H_{11})_3$..	265—267°	0·864

The author has attempted to prepare ethereal salts of orthocarbonic acid by the action of carbon tetrachloride on several sodium alcoholates, but the experiments have proved unsuccessful except in the case of sodium ethylate. W. C. W.

Decomposition of Dichloracrylic Acid by Alkalis. By O. Wallach and O. Bischof (*Deut. Chem. Ges. Ber.*, **12**, 57—60).—The formation of spontaneously inflammable chloracetylene by the action of alkalis on dichloracrylic acid takes place in two stages. Chloropropiolic acid, $CCl : C.COOH$, is probably first formed, which splits up into carbonic anhydride and chloracetylene, $CCl : CH$.

The authors wished to prepare a phenylated chloracetylene from phenyldichlorolactic acid, $CCl_2H.C(C_6H_5)(OH).COOH$, but they were unable to obtain this acid from bromacetophenone, since this body does

not form an addition-product with hydrocyanic acid, but is decomposed by it, forming carbonic oxide, ethyl bromide, benzaldehyde, and mandelic acid. W. C. W.

Acids obtained by the Saponification of Roman Chamomile Oil. By H. Kopp (*Liebig's Annalen*, **195**, 81—92).—The author saponified the oil by boiling it with alcoholic potash. After distilling off the alcohol the soap was boiled, first with water and then with dilute sulphuric acid, until nothing but water passed over. The distillate was neutralised with sodium carbonate and evaporated to dryness, and the residue decomposed by sulphuric acid. The oily mixture of acids thereby set free was finally submitted to fractional distillation. In this way the author found angelic and tiglic acids in about equal quantities, isobutyric acid in much smaller amount, and a fourth acid, most probably methacrylic acid, but this was not isolated. No other acid was present in appreciable quantity.

Angelic acid, $C_5H_8O_2$, melts at 45—45·5°, and boils at 185° (not at 191°, as formerly stated). Its *calcium salt*, $(C_5H_7O_2)_2Ca + 2H_2O$, is much more freely soluble in cold than in hot water. On heating a cold saturated solution, the salt crystallises in long brilliant needles, which disappear as the liquid cools. The *barium salt*, $(C_5H_7O_2)_2Ba + 4\frac{1}{2}H_2O$, is very freely soluble in water, and crystallises with difficulty. The *silver salt*, $C_5H_7O_2Ag$, is a white precipitate, which crystallises from boiling water in colourless feathery crystals. The *potassium salt* is crystalline, very soluble, and deliquescent.

Tiglic acid, $C_5H_8O_2$, melts at 64·5°, and boils at 198·5°. The *calcium salt*, $(C_5H_7O_2)_2Ca + 3H_2O$, crystallises in white laminæ, which dissolve sparingly in cold and freely in boiling water. The *barium salt*, $(C_5H_7O_2)_2Ba + 4H_2O$, is more soluble than the calcium salt, but much less soluble than the corresponding salt of angelic acid. It forms small hard prismatic crystals. The *silver salt* is less soluble than that of angelic acid, but may be crystallised from boiling water in small white feathery groups. The *potassium salt* crystallises readily in tufts of small needles, which are not deliquescent.

Conversion of Angelic Acid into Tiglic Acid.—The transformation of angelic acid into the isomeric tiglic acid by the action of heat or of concentrated sulphuric acid was observed by Demarçay (*Compt. rend.*, **83**, 906), whose statements are fully confirmed by the author. A quantity of pure angelic acid, after being kept in a state of gentle ebullition for 40 hours, was found to be almost entirely transformed into tiglic acid. J. R.

Constituents of Roman Chamomile Oil. By Köbig (*Liebig's Annalen*, **195**, 92—108). — The author submitted the oil to very careful fractional distillation, whereby he succeeded in separating it into five distinct portions, boiling at the following temperatures:—(1), 147—148°; (2), 177—177·5°; (3), 200—201; (4), 204—205; (5), above 220°, with decomposition. Each of these portions was analysed and saponified with aqueous potash, and the products of saponification were examined. The first portion was found to consist mainly of an ethereal salt of isobutyric acid, most probably ethyl isobutyrate. The

second portion consisted of the isobutyl salt of angelic acid, $C_5H_7O.O.C_4H_9$. The third and fourth portions were found to be the amyl salts of angelic and tiglic acids, angelic acid predominating in the former portion and tiglic acid in the latter. The fifth portion yielded by saponification angelic and tiglic acids and the two following bodies:—(*a*). A hexyl alcohol of sp. gr. 0·8295 at 15°, boiling at 152—153°, insoluble in water, and yielding a capronic acid by oxidation. This is believed by the author to be one of the eight theoretically possible primary hexyl alcohols, of which normal hexyl alcohol is the only one previously known. (*b*.) A thick colourless liquid boiling at 213·5 to 214·5°, of peculiar camphor-like odour, isomeric with ordinary camphor, and termed *anthemol* by the author. This body was found to be the hydroxyl-derivative of terpene. It exists in chamomile oil as an ethereal salt of angelic and tiglic acids. It reacts with acetic anhydride to form an ethereal salt, $C_{10}H_{15}O.C_2H_3O$, from which it is recovered unaltered by saponification.

According to these results, Roman chamomile oil consists of a mixture of isobutyl isobutyrate, isobutyl angelate, amyl angelate and tiglate, and the angelic and tiglic ethers of a new hexyl-alcohol and of terpene-alcohol (anthemol). Other substances, if present at all, can only exist in very small quantities. J. R.

Angelic and Tiglic Acids. By A. Pagenstecher (*Liebig's Annalen*, **195**, 108—128).—*Separation.*—To separate these acids, the author takes advantage of the peculiar behaviour of their calcium salts. Calcium angelate is more soluble in cold water than in hot: calcium tiglate, on the contrary, is more soluble in hot water than in cold. When, therefore, a concentrated cold solution of the two salts is heated to 60° or 70°, calcium angelate is thrown down, whilst calcium tiglate remains in solution. By appropriate application of these facts it is possible to separate nearly the whole of a mixture of the two acids in the form of pure calcium salts, from which the acids are liberated by addition of hydrochloric acid.

Action of Hydrobromic Acid.—Pure tiglic acid dissolves readily in concentrated hydrobromic acid, forming a clear solution which, after standing for a few days, deposits crystals of *bromhydrotiglic acid*, $C_5H_9BrO_2$. This substance crystallises from carbon bisulphide in large transparent tabular crystals having a brilliant lustre. It melts at 66—66·5°. It is insoluble in cold, and is decomposed by hot water.

Angelic acid, when treated with hydrobromic acid, yields a product identical with that obtained from tiglic acid, but in smaller quantity, tiglic acid yielding 80 per cent., whilst angelic acid yields only 60—70 per cent. of the theoretical amount of the brominated acid. At the same time, angelic acid yields other products, which are not formed in the reaction with tiglic acid.

Bromhydrotiglic acid dissolves easily in an aqueous solution of sodium carbonate, displacing carbonic acid, but the salt thereby formed speedily breaks up in the manner indicated by the equation:

$$C_4H_8Br.COONa = C_4H_8 + CO_2 + NaBr,$$

the products being *pseudobutylene*, carbonic anhydride, and sodium bromide.

Bromhydrotiglic acid, when boiled with water, is for the most part resolved into tiglic and hydrobromic acids, but a small portion is decomposed in the same manner as in the reaction with sodium carbonate: $C_5H_9BrO_2 = C_4H_8 + CO_2 + HBr$.

Bromhydrotiglic acid, when treated with sodium-amalgam (care being taken to keep the solution as nearly neutral as possible) yields *hydrotiglic acid*, $C_5H_{10}O_2$. This substance is a mobile colourless liquid, smelling like ordinary valeric acid but much fainter. It boils at 177° and remains liquid at 190°. Its sp. gr. at 21° = 0·941. The *calcium salt*, $(C_5H_9O_2)_2Ca + 5H_2O$, crystallises readily in long colourless needles, which effloresce in the air. The *silver salt* is a bulky white precipitate, soluble in boiling water, from which it crystallises in feathery forms. The *ethyl salt*, $C_4H_9.COOEt$, formed by heating a solution of the acid in absolute alcohol with concentrated sulphuric acid, is a colourless mobile liquid of agreeable fruity odour, boiling at 133·5°.

Together with hydrotiglic acid there is formed another acid having apparently the formula $C_{10}H_{18}O_4$, but this body has not been satisfactorily investigated.

Action of Bromine.—Tiglic acid dissolved in carbon bisulphide combines slowly with bromine to form *dibromhydrotiglic acid*, $C_5H_8O_2Br_2$, a solid crystalline substance melting at 86—86·5°. Angelic acid, under the same conditions, yields the same body, but in smaller quantity and accompanied by other products.

Dibromhydrotiglic acid, when heated with water in sealed tubes, is for the most part resolved into monobromobutylene, hydrogen bromide, and carbonic anhydride. The same reaction takes place at the ordinary temperature on dissolving the dibromo-acid in an aqueous solution of sodium carbonate.

Dibromhydrotiglic acid is converted into tiglic acid by the action of sodium-amalgam. J. R.

Constitution of Tiglic and Angelic Acids. By Fittig (*Liebig's Annalen*, **195**, 128—130).—Tiglic acid has recently been shown by Schmidt and Berendes (*Annalen*, **191**, 94) to be identical with methylcrotonic acid, the accepted formula of which is—

$$CMeH : CMe.COOH.$$

The observations of Kopp, Köbig, and Pagenstecher, as detailed in the foregoing papers, are all in accord with this formula. The derivatives of tiglic acid described by Pagenstecher may be formulated as follows:—

Hydrotiglic acid	$CMeH_2.CMeH.COOH$.
Bromhydrotiglic acid	$CMeH_2.CMeBr.COOH$.
Dibromhydrotiglic acid ..	$CMeHBr.CMeBr.COOH$.

The constitution of angelic acid remains an open question, no sufficient light being thrown upon it, or upon the relation of the two isomeric acids to each other, by these researches. J. R.

Bromocitraconic Acid. By E. Bourgoin (*Compt. rend.*, **88**, 343—346).—Kekulé has shown that citraconic acid unites with two atoms of bromine, forming dibromopyrotartaric acid, from the lime salt of which monobromocrotonic acid is obtained by boiling with water, $C_5H_6Br_2O_4 = HBr + CO_2 + C_4H_5BrO_2$. Cahours has shown that this reaction takes place in two stages: at first carbonic anhydride is eliminated and an isomeride of dibromobutyric acid formed, $C_5H_6Br_2O_4 = CO_2 + C_4H_6Br_2O_2$. This new acid when saturated with a dilute solution of potash and boiled for a few minutes, gives monobromocrotonic acid. The author has endeavoured to obtain a homologue of tartaric acid isomeric or identical with the citratartaric acid of Carius, by removing the bromine from dibromopyrotartaric acid by means of silver oxide: $C_5H_6Br_2O_4 + 2Ag(HO) = 2AgBr + C_5H_8O_6$. This reaction, however, is not realised, only half the bromine being removed from the dibromopyrotartaric acid by moist silver oxide. When a concentrated solution is employed, the liquid becomes hot, carbonic anhydride is evolved, and on cooling the filtered liquid deposits crystals of the bromocrotonic acid of Kekulé: $C_5H_6Br_2O_4 + Ag(HO) = AgBr + H_2O + CO_2 + C_4H_5BrO_2$.*

When, however, a dilute and cold solution of the dibromopyrotartaric acid is employed, and the filtrate from the silver bromide is evaporated, a new acid is obtained which the author calls *bromocitraconic acid*, $C_5H_6Br_2O_4 = HBr + C_5H_5BrO_4$.

Bromocitraconic acid is very soluble in water; its solution, concentrated in the cold, gives a colourless, unstable, uncrystallisable liquid, soluble in alcohol and ether. It is bibasic, and forms salts with the alkalis and alkaline earths which are soluble in water and tend to decompose with formation of a metallic bromide, their neutral solutions becoming acid on evaporation.

The potassium salt, obtained in a pure state by evaporation of its solution over sulphuric acid under a bell-jar, is crystalline, granular, and deliquescent. The silver salt is obtained as a white precipitate, which rapidly turns yellow with formation of silver bromide. Analyses of the potassium and silver salts are given. J. M. H. M.

Tetric Acid and its Homologues. By E. Demarçay (*Compt. rend.*, **88**, 126—128).—*Tetric acid*, $3C_4H_4O_2 + H_2O$, is a colourless body crystallising from its aqueous solution in triclinic prisms, sparingly soluble in cold water. It dissolves readily in hot water, alcohol, ether, and a hot mixture of chloroform and alcohol, but is insoluble in chloroform. It melts at 189°, and like its homologues, gives a violet-red colour with ferric chloride.

Pentic acid, $3C_5H_6O_2 + H_2O$, melts at 127—128°, and crystallises in orthorhombic crystals, having their cleavage parallel to P. It is very soluble in hot chloroform, but only slightly so in the cold.

Hexic acid, $3C_6H_8O_2 + H_2O$, prepared from ethyl acetopropylacetate, crystallises in large pearly plates from a boiling aqueous solution. It melts at 126°.

* Misprinted in the original paper (C = 6) as $C_{10}H_6Br_2O_8 + AgHO_2 = AgBr + H_2O_2 + C_2O_4 + C_{10}H_5BrO_4$.—J. M. H. M.

Isohexic acid, $3C_6H_8O_2 + H_2O$, is obtained from ethyl aceto-isopropylacetate. It crystallises from its ethereal solution in orthorhombic prisms, which melt at 124°.

Heptic acid, $3C_7H_{10}O_2 + H_2O$, the author has previously described.

These bodies resemble one another very closely in their chemical properties. On dry distillation, a portion passes over undecomposed below 200°, leaving a carbonaceous residue.

They form remarkable salts, the radicle, $C_4H_4O_2$, &c., acting like silica, several molecules uniting with one or more molecules of a base. Thus, if A represents the acid radicle and B a base (BaO, CaO, MgO), salts of the following constitution may be obtained: 2A + B, 3A + B, 5A + 2B. By the action of fuming nitric acid, they yield nitro-derivatives: they dissolve in sulphuric acid without decomposition even at 100°. When treated with chlorine or bromine, they form additive compounds which are not decomposed by water. Nascent hydrogen is without action.

By the action of phosphorus pentachloride on tetric acid an oily chlorinated product was obtained $(3C_4H_4O_2 + H_2O) + 4PCl_5 = 2HCl + 4PCl_3O + 3C_4H_4Cl_2O$. The oil is separated from the other products by treatment with water, in which it is insoluble. It has a feeble aromatic odour, boils at 171—172° with slight decomposition, and its sp. gr. at 10° is 1·471. It unites readily with bromine or chlorine, forming the compounds $C_4H_4Cl_2Br_2O$, m. p. 67—67·5°, and $C_4H_4Cl_4O$, m. p. 48—48·5°. These are crystalline bodies, which are not decomposed by water, alcohol, ammonia, or potash, and probably are chlorobrom- and tetrachlor-acetones. Fuming nitric acid dissolves $C_4H_4Cl_2O$, forming a nitro-acid. It is also dissolved by sulphuric acid, giving rise to a purple colour.

The homologues of tetric acid form analogous compounds, resembling $C_4H_4Cl_2O$ in their chemical and physical properties. $C_5H_6Cl_2O$ boils at 189—192°, decomposing at the same time. The other homologues are not volatile without decomposition.

As the vapour-densities of tetric acid and its derivatives have not been determined, it is possible that their formulæ may be multiples of those given.

Tetric acid and its homologues are decomposed by concentrated caustic potash at 150°, according to the equation $C_4H_4O_2 + 2KOH = C_3H_5KO_2 + CHKO_2$. L. T. O'S.

Homologues of Oxyheptic Acid. By E. Demarçay (*Compt. rend.*, **88**, 289—291).—The author has prepared the following:—

Oxytetric acid, $3C_4H_4O_3 + H_2O$ (m. p. 203—204°), crystallises from boiling water in small rounded masses formed of minute needles. By slow evaporation of its alcoholic solution, crystals belonging to "one of the last three systems" are formed. This acid is very soluble in boiling water, alcohol, and ether, but is insoluble in chloroform, as are its homologues.

Oxypentic acid, $3C_5H_6O_3 + H_2O$ (m. p. 193°), behaves with boiling water like the preceding, but is less soluble in cold water, and its crystalline form is different.

Oxyhexic acid, $3C_6H_8O_3 + H_2O$ (m. p. 173—174°), derived from ethyl propylacetoacetate. It separates from its solution in boiling water in very small nacreous plates.

Isoxyhexic acid (m. p. 186—187°), isomeric with the preceding, and derived from ethyl isopropylacetoacetate. Its alcoholic solution yields fine clinorhombic crystals by evaporation.

All these acids easily decompose carbonates. Their salts correspond with the formula (for oxytetric acid) $3C_4H_3M'O_3 + M_2'O$, and are generally well crystallised. The copper and silver salts are but slightly soluble in water.

The acids are easily converted into ethereal salts by treatment with alcohol at 150°. Nascent hydrogen is fixed by them thus: $(3C_4H_4O_3 + 3H_2O) + H_2 = 3C_4H_6O_3 + H_2O$. The *hydroxytetric acid*, thus obtained (m. p. 111°) crystallises easily in indistinct masses, and is very soluble in water, alcohol, and ether. Its homologues are less and less soluble in cold water. These bodies on treatment with alcohol at 150° are converted into ethereal salts of feeble and agreeable odours.

Phosphorus pentachloride reacts on oxytetric acid and its homologues, thus: $(3C_4H_4O_3 + H_2O) + 7PCl_5 = 7POCl_3 + 5HCl + 3C_4H_3Cl_3O$.

The chlorinated oils from the higher homologues are attacked by water with difficulty, but the oxytetric chloride is attacked easily by cold water. These chlorides cannot be distilled at the ordinary pressure without decomposition. They react with alcohol in two stages, the first being represented by $C_4H_3Cl_3O + 2C_2H_6O = 2HCl + C_4H_3ClO(OC_2H_5)_2$. This reaction takes place on dissolving the chloride in a large excess of cold alcohol; if ammonia be then added, the following reaction occurs: $C_4H_3ClO(EtO)_2 + NH_3 = HCl + C_4H_3(NH_2)O(EtO)_2$. This amidated ethereal salt crystallises easily in large satiny needles, slightly soluble in cold water.

The second stage of the action of alcohol on these chlorides is represented thus: $C_4H_3ClO(EtO)_2 + EtHO = C_4H_3O(EtO)_3 + HCl$; and, if the alcohol contains water this also occurs, $C_4H_3OCl(EtO)_2 + H_2O = C_4H_3O(HO)(EtO)_2 + HCl$. This last ethereal salt is also produced in a state of purity by prolonged boiling of the amidated ethereal salt with water.

The author had wrongly attributed the formula $C_7H_9(HO)O(EtO)_2$ to some oxyheptic ether, $C_7H_9O(EtO)_3$, which contained some of the ether, $C_7H_9O(HO)(EtO)_2$, as an impurity.

These ethereal salts when treated with aqueous ammonia ultimately yield an amide which is also obtained as the final product of the action of aqueous ammonia on the chloride of the corresponding acid:

$$3C_4H_3Cl_3O + 2H_2O + 5NH_3 = 9HCl + C_{12}H_9(NH_2)_5O_5.$$

This body, $C_{12}H_9(NH_2)_5O_5$, is the true amide of oxytetric acid, for $C_{12}H_9(OH)_5O_5 = 3C_4H_4O_3 + H_2O$. J. M. H. M.

Relations of Tetric and Oxytetric Acids and their Homologues to Succinyl, Malyl, and other Radicles of the Bibasic Acids. By E. Demarçay (*Compt. rend.*, **87**, 351—343).—The author considers that the reactions already described by him justify the for-

mulæ $3C_4H_4O_2 + H_2O$ and $3C_4H_4O_3 + H_2O$, which he has assigned to tetric and oxytetric acids respectively. He regards the radicles, $C_4H_4O_2$, &c., as similar to silicic and tungstic anhydrides since they combine with bases in the proportion of several molecules of the radicle to one or more molecules of base. In the present paper he shows the constitution of the radicle $C_4H_4O_2$ to be $\begin{matrix}CH_2—CH_2\\ |\quad\quad |\\ CO\ —CO\end{matrix}$, which is the formula of *succinyl*, the radicle of succinic acid. The radicle, $C_4H_4O_3$, of oxytetric acid will then be $\begin{matrix}CH_2—CH.HO\\ |\quad\quad |\\ CO\ —CO\end{matrix}$, which is the formula of *malyl*, the radicle of malic acid.

These constitutional formulæ are inferred from the reactions of phosphorus pentachloride, potash, and bromine, on tetric and oxytetric acids. In the higher homologues of these acids hydrogen is replaced by methyl, ethyl, &c.

The author remarks that these bodies demonstrate the existence of a closed and saturated chain of 4 carbon atoms, which nevertheless resembles the so-called unsaturated bodies derived from ethylene, in the facility with which it fixes chlorine and bromine.

J. M. H. M.

Synthesis of Uric Acid Derivatives. By E. Grimaux (*Compt. rend.*, **88**, 85—87).—As the author has already shown (this vol., p. 375), by acting with phosphorus oxychloride on a mixture of urea and malonic acid, a yellow amorphous mass is obtained, which by the successive action of nitric acid and sulphuretted hydrogen yields alloxantin. The amorphous mass is a mixture of malonyl urea (barbituric acid), $C_4H_4N_2O_3$, with a yellow amorphous substance slightly soluble in water, the equation representing the reaction being—

$$3C_3H_4O_4 + 3CO(NH_2)_2 + 2POCl_3 = 3C_4H_4N_2O_3 + 2H_3PO_4 + 6HCl.$$

The malonyl urea is separated from the amorphous body by treatment with alcohol, and recrystallisation from water. It is thus obtained in transparent efflorescent crystals, losing their water of crystallisation at 100°, and showing all the characteristic reactions pointed out by Baeyer; thus by the action of nitric acid, it yields dilituric acid (nitrobarbituric acid) $C_4H_3(NO_2)N_2O_3$; when treated with potassium nitrite, it yields potassium violurate (nitroso-barbituric acid); and by the action of bromine, dibromobarbituric acid. The author has prepared ammonium thionurate, uranil (amidobarbituric acid), and alloxantin, from the malonyl urea.

The yellow amorphous compound appears to be a condensation product of malonyl urea, as it can be obtained by treating malonyl urea with phosphorus oxychloride, and when heated with bromine at 100° C. it yields dibromo-barbituric acid.

By treating tartronic acid (oxymalonic acid) $C_4H_4O_3$ in a similar manner, other uric acid derivatives are formed, probably dialuric acid (oxymalonyl urea) $C_4H_4N_2O_4$.

This reaction serves as a test for the presence of malonic and oxy-

malonic acid, for by treating a small quantity of either acid with urea and phosphorus oxychloride, and evaporating the product to dryness with nitric acid, and adding ammonia to the residue, the purple colour of murexide is obtained. L. T. O'S.

Compounds of the Uric Acid Group. By J. Ponomareff (*Bull. Soc. Chim.* [2], **31**, 70).—Allantoïc acid, the hydantoïc acid of Mulder, prepared by dissolving allantoïn in potash solution and precipitating by dilute sulphuric acid, has the formula $C_4H_8N_4O_4$. By the action of boiling water it is decomposed into allanturic acid, $C_3H_4N_2O_3$, and urea. Allantoxanic acid is prepared by the oxidation of allantoïn in alkaline solution: $C_4H_6N_4O_3 + O + KHO = C_4H_2KN_3O_4 + NH_3 + H_2O$. Boiling water decomposes this acid with elimination of carbonic anhydride and formation of the compound $C_3H_3N_3O_2$, which the author proposes to call *allantoxoïdin*.

Allantoxoïdin separates from aqueous solutions in prismatic crystals containing 1 mol. H_2O. It is decomposed by heat without fusion, giving off hydrocyanic acid; it dissolves readily in boiling water, less easily in cold water and in alcohol, and is insoluble in ether. It forms unstable salts with alkalis. The action of sodium amalgam converts it into hydroxanic acid, $C_8H_{10}N_6O_7$; this forms stable salts.

R. R.

Compounds of Aluminium Chloride with Benzene and Toluene. By G. Gustavson (*Bull. Soc. Chim.*, **31**, 71).—With benzene and toluene aluminium chloride forms compounds, which are the analogues of those formed by aluminium bromide, $Al_2Cl_6.6(C_6H_6)$, (sp. gr. 1·14 at 0°) and $Al_2Cl_6.6(C_7H_8)$ (sp. gr. 1·08 at 0°). They are rather viscous, slightly orange-coloured liquids, which water partially decomposes, regenerating benzene and toluene. At a low temperature the former solidifies to a crystalline mass (m. p. 3°). Bromine, carbon chloride, isobutyl chloride, and amyl chloride act very energetically on these compounds with separation of hydrochloric acid.

R. R.

Compounds of Cobalt and Nickel Chlorides with Anilines. By E. Lippmann and G. Vortmann (*Deut. Chem. Ges. Ber.*, **12**, 79—82).—The following compounds, containing 1 mol. of nickel or cobalt chloride and 2 mols. of aniline or toluidine, were prepared by adding an alcoholic solution of the metallic chloride to the base.

Aniline forms with cobalt chloride pale-red crystals containing 2 mols. of alcohol of crystallisation, and also blue crystals containing no alcohol. With nickel chloride, aniline forms an apple-green compound containing 2 mols. of alcohol which are expelled at 100°.

Paratoluidine cobalt chloride crystallises in glistening blue needles; the toluidine nickel chloride is green.

Xylidine cobalt chloride forms small pale-blue crystals.

W. C. W.

Succinyl Compounds of Toluidine. By G. v. Becchi (*Deut. Chem. Ges. Ber.*, **12**, 25).—Toluylsuccinimide, $C_{11}H_{11}O_2N$, or $C_2H_4 : (CO)_2 : N.C_6H_4.CH_3$, is obtained by distilling a mixture of equivalent quantities of orthotoluidine and succinic acid. The distillate, purified by fractionation, is washed with a small quantity of

ether, and finally recrystallised from that solvent. The pure substance forms glistening needles (m. p. 75°, b. p. 345°).

W. C. W.

Amylideneaniline. By E. Lippmann and W. Strecker (*Deut. Chem. Ges. Ber.*, **12**, 74—76).—*Amylideneaniline*, $(C_6H_5)(C_5H_{10})''N$, separates out, on the addition of aniline to valeraldehyde. It is deposited from a hot ethereal solution in golden monoclinic crystals, in which $a : b : c = 0{\cdot}5602 : 1 : 0{\cdot}4972$ and $ac = 69°{\cdot}27$. This substance melts with decomposition at 97°, and forms a flesh-coloured platinochloride with platinum tetrachloride. W. C. W.

Paraphenylenediamine. By A. Krause (*Deut. Chem. Ges. Ber.*, **12**, 47—56).—On adding a solution of bleaching-powder in excess to paraphenylenediamine hydrochloride dissolved in water and acidified with hydrochloric acid, a yellowish-white crystalline precipitate separates out, which has the composition $C_6H_2Cl_2(NH)_2$. This substance dissolves in alcohol, ether, benzene, and glacial acetic acid; it is also sparingly soluble in hot water. When slowly heated in an oil-bath, it detonates at 124°, but if rapidly heated it may be melted without undergoing decomposition. It is converted into phenylenediamine hydrochloride by the action of reducing agents. Hydrochloric acid (sp. gr. 1·2) converts the compound $C_6H_4Cl_2N_2$ into a substance crystallising in pale-red needles (m. p. 218°), having the composition $C_6H_6Cl_4N_2$, or $C_6H_4Cl_4N_2$. (Hydrobromic acid appears to form a similar compound with $C_6H_4Cl_2N_2$.) The red needles are insoluble in water and in cold hydrochloric acid, but dissolve freely in alcohol, benzene, ether, and glacial acetic acid. It is converted into chloranil by the action of nitric acid. Chloranil may be prepared by passing chlorine into a solution of paraphenylenediamine in glacial acetic acid.

Dichlorodibromoquinone, $C_6Cl_2Br_2O_2$, separates out in bronze-coloured rhombic plates, when a glacial acetic acid solution of the compound, $C_6H_4Cl_2N_2$, is treated with bromine and water.

$C_6H_4Cl_2N_2 + Br_4 + 2H_2O = 2NH_4Br + C_6Cl_2Br_2O_2$. On reduction with stannous chloride the corresponding quinol (hydroquinone) is obtained in broad needles soluble in alcohol. When heated to 220° it turns brown, and melts at 230°.

Monochloromonobromanilic acid, $C_6H_2ClBrO_4$.—The sodium salt, $C_6ClBr(ONa)_2O_2 + 4H_2O$, is obtained by the action of dilute soda on dichlorodibromoquinone. By the addition of hydrochloric acid to a solution of the sodium salt, the free acid is precipitated either as a red anhydrous powder, or in pale-red crystalline scales containing 1 mol. of water. The barium and silver salts of this acid are insoluble in water. W. C. W.

Synthesis of Carbotriphenyltriamine. By W. Weith (*Deut. Chem. Ges. Ber.*, **12**, 101—108).—By the action of phosphorus trichloride on a mixture of aniline and paranitrobenzoic acid at 180°, the compound $C_6H_4NO_2.C(NC_6H_5)(NHC_6H_5)$ is formed, which, on reduction with tin and hydrochloric acid, yields carbotriphenyltriamine, $(C_6H_4.NH_2)(NH.C_6H_5) : NC_6H_5$ (m. p. 196°). This base is decom-

posed into aniline and paramidobenzoic acid when heated with a mixture of equal volumes of fuming hydrochloric acid and water at 155—160°. W. C. W.

Constitution of the Rosanilines. By A. Rosenstiehl (*Bull. Soc. Chim.* [2], **31**, 13—20).—The author reviews the researches of E. and O. Fischer on the constitution of rosaniline (*Annalen*, **194**, 242), and compares their conclusions with the results of his own investigations. He infers that there are no rosanilines which have more than 20 atoms of carbon in their molecule, and that there exist three modifications of rosaniline which are thus characterised :—

1. α-Rosaniline splitting up into aniline and paratoluidine, and into the constitution of which it has been proved by the Fischers that only one molecule of toluidine enters.

2. β-Rosaniline splitting up into aniline and orthotoluidine. This might have been called orthorosaniline. It has not been examined by the Fischers, but has by them been confounded with the next named rosaniline.

3. αβ-Rosaniline, or Hofmann's rosaniline, splitting up into aniline, orthotoluidine, and paratoluidine.

The author at first regarded the last-named rosaniline as a mixture of the other two, but he afterwards recognised that it was a well-defined compound, and the Fischers have just proved that it is in reality the superior homologue, and not the isomeride of pararosaniline. The second rosaniline can only be an isomeride of the first or of the third. As it contains the grouping of only one toluidine molecule, it is probably an isomeride of pararosaniline; but this can only be definitely decided by experiment. In any case, whether it contain 19 or 20 atoms of carbon, its study will show that, contrary to received opinions, the existence of isomeric rosanilines is not impossible.

R. R.

Perchlorophenol Chloride. By F. Beilstein (*Deut. Chem. Ges. Ber.*, **11**, 2182—2183).—This compound is formed by passing an excess of chlorine into an acetic acid solution of metachloracetanilide. The product is precipitated with water, and the precipitate extracted with dilute acetic acid; the insoluble residue is then treated with carbon bisulphide to dissolve the chloride, which may be obtained in crystals on evaporation of the bisulphide. By washing with alcohol and recrystallisation from light petroleum, perchlorophenol chloride, C_6Cl_7HO, is obtained in large colourless prisms (m. p. 78·5—80°). It is easily soluble in benzene, carbon bisulphide, and alcohol, but only slightly soluble in acetic acid. Alkalis decompose it entirely; when heated at 230° with alcohol it yields pentachlorophenol, C_6Cl_5OH (m. p. 183—184°).

Perchlorophenol chloride is analogous to Lallemand's pentachlorthymol (*Jahrb.*, 1856, 519). Since this latter body yields on heating propylene and trichlorocresol, its constitution must be

$$(OH)C_6Cl_3(CH_3)(C_3H_7)Cl_2.$$

The author concludes, therefore, that the formula of the thymol derivative is $C_{10}H_{11}Cl_5O$, and not, as Lallemand supposed, $C_{10}H_9Cl_5O$.

P. P. B.

Nitrocuminol and its Derivatives. By E. Lippmann and W. Strecker (*Deut. Chem. Ges. Ber.* **12**, 76—79).—*Nitrocuminol* prepared by nitrating pure cuminol (b. p. 222° corr.), forms yellow monoclinic crystals, which melt at 54°. On oxidation with potassium dichromate and sulphuric acid it yields *nitrocuminic acid*, $C_6H_3(NO_2)(C_3H_7).COOH$ (m. p. 158°) identical with the compound obtained by nitrating pure cuminic acid.

Dinitrocuminic acid, $C_6H_2(NO_2)_2(C_3H_7).COOH$, is obtained in red crystals by adding cuminic acid to a mixture of nitric and sulphuric acids. W. C. W.

Derivatives of Quinol (Hydroquinone). By R. Nietzki (*Deut. Chem. Ges. Ber.*, **12**, 38—42).—Mononitrodiethoxyquinol, prepared by mixing a solution of diethoxyquinol in 5 parts of glacial acetic acid, with an equal volume of nitric acid, sp. gr. 1·25, crystallises from an alcoholic solution in golden needles (m. p. 49°). By treating the solution of this nitro compound in alcoholic potash with a small quantity of zinc-dust, there is formed a mixture of a hydrazo-derivative crystallising in colourless needles, and an azo-derivative crystallising in red plates. The two substances are separated by digesting with warm dilute hydrochloric acid, which dissolves out the former. The azo-compound, $(EtO)_2C_6H_3.N : N.C_6H_3(EtO)_2$, is soluble in ether, benzene, and in hot alcohol. It dissolves in strong hydrochloric and sulphuric acids, forming violet solutions, from which it is re-precipitated on the addition of water. It melts at 128°, and distils at a higher temperature. The hydrochloride of the base obtained by evaporating the solution of the hydrazo-derivative in hydrochloric acid has the composition $NH.C_6H_2(EtO)_2.C_6H_2(EtO)_2.NH_2(HCl)_2$. It crystallises in colourless silky needles which are sparingly soluble in hot water, and almost insoluble in strong hydrochloric acid. The free base is deposited from an alcoholic solution in colourless plates (m. p. 129°).

Mononitrodiethoxyquinol yields two dinitro-derivatives, $C_6H_2(NO_2)_2(EtO)_2$, viz., one melting at 176° (*Ber.*, **11**, 1448) and another melting at 130°; the latter is freely soluble in alcohol.

A compound, having the composition $C_{10}H_{13}N_3O_2$, was obtained by the action of nitrous acid on the amido-derivative of diethoxyquinol, $C_{10}H_{12}(NH_2)_2O_2 + HNO_2 = C_{10}H_{13}N_3O_2 + 2H_2O$. This compound crystallises in colourless needles (m. p. 233°), soluble in hot alcohol and in glacial acetic acid. It also dissolves in solutions of the caustic alkalis, but is reprecipitated on the addition of acids.

W. C. W.

Pentabromoresorcinol. By R. Benedikt (*Deut. Chem. Ges. Ber.*, **11**, 2168—2172).—By the action of sodium-amalgam on pentabromoresorcinol, bromoform is produced; tin and hydrochloric acid remove the bromine from pentabromoresorcinol, the reaction taking place in two stages; in the first, tribromoresorcinol is produced, which is finally converted into resorcinol (resorcin).

When 3 mols. of pentabromoresorcinol and 2 mols. aniline are heated together, a mixture of tribromoresorcinol and tribromaniline is formed; these compounds may be separated by the difference of solubility in

water. Phenol acts in a manner similar to aniline, the reaction taking place as follows :—

$$3Br_2C_6Br_3HO_2 + 2C_6H_5.NH_2 = 3C_6Br_3H_3O_2 + 2C_6Br_3H_2.NH_2.$$
$$3Br_2C_6Br_3HO_2 + 2C_6H_5.OH = 3C_6Br_3H_3O_2 + 2C_6Br_3H_2.OH.$$

Attempts to convert tribromoresoquinone into resorcinol have been unsuccessful. The former compound, when treated with tin and HCl, yields an amorphous insoluble mass, from which, by treating with glacial acetic acid, a compound is obtained crystallising in red silky needles soluble in alcohol and ether. This compound, when heated to 230°, becomes brown, and at 280° decomposes with partial fusion. The formula for this compound may be either $C_6Br_2H_4O_2$, or $C_{12}Br_4H_6O_4$; in the latter case it may either be tetrabromoresoquinhydrone, $C_6Br_2H_2(OH).O.O.C_6Br_2H_2(OH)$, or tetrabromodiresorcinol, $C_6Br_2H(OH)_2.C_6Br_2H(OH)_2$. The fact that the new compound yields diphenyl on distillation with zinc-dust, and that by the action of sodium-amalgam it does not yield resorcinol, would render the second formula the more probable. P. P. B.

Action of Nitrous Acid on Resorcinol Ethers. By B. Aronheim (*Deut. Chem. Ges. Ber.*, **12**, 30—32).—*Ethoxymononitrosoresorcinol*, $C_6H_3(NO)(OC_2H_5).OH$, separates out as a yellow precipitate on the gradual addition of a solution of nitrogen trioxide in sulphuric acid, to diethoxyresorcin dissolved in acetic acid. After the mixture has remained at rest for two hours the precipitate is collected on a filter, dissolved in a dilute solution of soda, and reprecipitated by an acid. This substance decomposes without melting at 180°. It is insoluble in the ordinary solvents, but it is dissolved by strong nitric acid with formation of a dinitro-product, $C_6H_2(NO_2)_2(OC_2H_5).OH$ crystallising in brilliant white needles (m. p. 75°), which dissolve in hot water. W. C. W.

Formation of Hydrocinnamic Acid by means of the Pancreas Ferment. By E. and H. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 107—108).—By the action of the pancreas ferment on flesh, butyric, valerianic, and phenylpropionic (hydrocinnamic) acids are formed. The authors think it possible that the occurrence of hippuric acid in the urine may be due to the decomposition of phenylpropionic acid. W. C. W.

Hydroxypropylbenzoic Acid. By R. Meyer and J. Rosicki (*Deut. Chem. Ges. Ber*, **11**, 2172—2174).—In continuing their investigation (*Ber.*, **11**, 1790) of this acid, the authors find that its methyl salt cannot be obtained by the ordinary methods, inasmuch as the acid loses 1 mol. H_2O in presence of hydrochloric acid, and the ethereal salt of hydroxypropenylbenzoic acid is obtained. By heating silver hydroxypropylbenzoate with methyl iodide, a small quantity of the methoxypropylbenzoate was obtained, as a liquid which is not volatile in aqueous vapour.

Acetic chloride and anhydride, like hydrochloric acid, resolve hydroxypropylbenzoic acid into the unsaturated acid, viz., hydroxypropenylbenzoic acid. The copper salt of this last-named acid has the composition $(C_{10}H_9O_2)_2Cu + 7H_2O$; the barium salt $(C_{10}H_9O_2)_2Ba +$

H_2O crystallises in white shining leaflets; and the ammonium salt $C_{10}H_9O_2.NH_4$ forms transparent plates.

By the dry distillation of calcium hydroxypropylbenzoate, a mixture of hydrocarbons, boiling at 140—150°, and a small quantity of a solid (m. p. 205°) was obtained. From the analysis and physical properties of this solid it appears to be paradiphenylbenzene; on oxidation it yields paradiphenylcarbonic acid (m. p. 215—217°).

Hydroxypropylbenzoic and hydroxypropenylbenzoic acids are converted by the action of concentrated hydrochloric acid into an isomeride of the latter. The new acid melts at 255—260°; the composition of its silver salt is $C_{10}H_9O_2Ag$; its barium salt has the same composition as barium hydroxypropenylbenzoate, viz., $(C_{10}H_9O_2)_2Ba + H_2O$, but differs from it in appearance. Bromine acts but slowly on the new acid, which is also unattacked by sodium-amalgam. The authors regard this behaviour of hydroxypropylbenzoic acid with hydrochloric acid as analogous to that of tropic acid, yielding under similar circumstances atropic and isatropic acids. P. P. B.

Amidobenzoic Percyanides. By P. Griess (*Deut. Chem. Ges. Ber.*, **11**, 2180).—The author wishes to substitute the following formulæ for those given in a former communication (this volume, p. 321).

I. Cyanogen and metamidobenzoic acid (*a*) in alcohol. Amidobenzoic percyanide $(CN)_2NH_2.C_6H_4.COOH$. Carbimidamidobenzoic acid, $HN:C(NH.C_6H_4.COOH)_2$; oxethylcarbimidamidobenzoic acid, $HN:C(EtO).NH.C_6H_4.COOH$. (*b*) in water. Amidobenzoic percyanide $(CN)_2NH_2.C_6H_4.COOH$; cyancarbimidamidobenzoic acid, $HN:C(CN)NH.C_6H_4.COOH$.

II. Cyanogen and orthoamidobenzoic acid. (*a*) in alcohol. Oxethylcyanamidibenzoyl, $(EtO)C<\begin{matrix}NH.C_6H_4.CO\\N\text{———}\end{matrix}$. (*b*) in water. Dicyanamidobenzoyl, $CN.C<\begin{matrix}NH.C_6H_4.CO\\N\text{———}\end{matrix}$. P. P. B.

Digallic Acid. By H. Schiff (*Deut. Chem. Ges. Ber.*, **12**, 33—38).—The author denies Freda's statement (*Ber.*, **11**, 346, 2033) that the digallic acid prepared by the action of arsenic acid on gallic acid is a compound of gallic acid and arsenic, and shows that after the arsenic has been completely removed, the substance still exhibits the reactions and properties of digallic acid.

The author also points out that the melting point of anhydrous gallic acid is 240° and not 210°, as generally stated. W. C. W.

Laurent's "Carminaphtha." By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 64—67).—Laurent formerly observed, studied, and analysed a substance, to which he gave the name of *carminaphtha*, but he failed to ascertain the conditions under which it was formed, and the substance was again lost, so to speak, although several other chemists have since met with it in the same accidental way. The author has succeeded in determining the conditions of its formation, so that it can now be obtained at pleasure. He dissolves 128 grams of naphtha-

lene by a gentle heat, in a sufficient quantity of glacial acetic acid, and adds a cold saturated solution containing 600 grams of chromic acid in the same solvent. The chromic solution is added gradually with gentle heating, until the mixture becomes green. When all the chromic solution has been added, the mixture is boiled for some minutes. The whole is then saturated by an alkali (hydrate or carbonate), and when the liquid is again acidulated, carminaphtha is precipitated in red or brownish-red flocks. If the alkaline liquid be filtered before acidulation, the chromium oxide which remains in the filter contains much carminaphtha, which can be separated by dissolving the oxide in acids.

Carminaphtha appears to be formed of two substances, which differ only by their shades of colour. It is very stable, and resists the action of many reagents. It dyes wool and silk without a mordant, of a deep, red-brown colour, and it imparts chamois tints more or less deep to cotton mordanted with metallic oxides. If, however, it should prove serviceable to the dyer, it will be less for the brilliancy or beauty of its tints than for their permanence.* R. R.

Hydrocarbon from Rosin Oil. By W. Kelbe (*Deut. Chem. Ges. Ber.*, **11**, 2174—2175).—When rosin oil is heated at 200° with sulphur, hydrogen sulphide and carbon oxysulphide are evolved, leaving a high boiling residue. On distilling this, a product is obtained, which solidifies on cooling, and crystallises from alcohol in white shining leaflets (m. p. 94—95°). Under similar circumstances, all terpenes appear to form high boiling hydrocarbons. The above compound is also formed when rosin oil is treated with phosphorus pentachloride; so that it would appear to be formed by dehydration, accompanied by a removal of carbon. This compound cannot be distilled without decomposition, the portion which passes over being a hydrocarbon, which crystallises from alcohol in needles (m. p. 86°).

The hydrocarbon from rosin oil appears to be different to the colophthalin $C_{11}H_{10}$, obtained by Curie (Staedel's *Jahresber.*, 1874) by heating sulphur and colophony together. P. P. B.

Lupinin, a New Glucoside. By E. Schulze and J. Barbieri (*Deut. Chem. Ges. Ber.*, **11**, 2200—2203).—This new glucoside occurs in *Lupinus luteus*. It has the composition $C_{29}H_{32}O_{16} + 7H_2O$, and is sparingly soluble in water and in alcohol. It dissolves easily in ammonia, forming yellow solutions, from which it is thrown down by acids as a yellow crystalline precipitate. Its ammoniacal solution darkens on exposure to the air, and gives a yellow precipitate with solution of lead acetate.

By heating with dilute mineral acids, lupinin is decomposed into a yellow insoluble body, and what appears to be dextrose; so that the decomposition of lupinin by dilute acid may be expressed thus:

$$C_{29}H_{32}O_{16} + 2H_2O = C_{17}H_{12}O_6 + 2C_6H_{12}O_6.$$

* The author, at the conclusion of the paper, makes some remarks on the probable formation of naphthaquinone by the oxidation of naphthalene by chromic acid in acetic acid solution, and appears to be quite unaware that this has already been done (Groves, *Chem. Soc. J.*, 1873, 209).

The yellow substance the author designates *lupigenin*. It is insoluble in water, and but sparingly soluble in spirits of wine. It dissolves in concentrated sulphuric acid, forming a yellow solution, which changes to a yellowish-red when nitric acid is added, and to a reddish-brown on adding potassium dichromate. Ammonia dissolves it easily, forming a deep yellow solution, from which acids precipitate the lupigenin as a yellow flocculent mass. When the ammoniacal solution is evaporated over sulphuric acid, an ammonium compound of lupigenin separates out as a citron-yellow crystalline powder, having the composition $C_{17}H_{11}O_6NH_4 + H_2O$.

Lupigenin melts to form a dark brown liquid, and at a higher temperature sublimes with partial decomposition as a yellow crystalline mass. P. P. B.

Naringin. By E. Hoffmann (*Arch. Pharm.* [3], **14**, 139—145).—Naringin, the hesperidin of de Vrij, which is found in the fully developed buds of *Citrus decumana* to the amount of 2 per cent., is obtained from the residue left on distillation of the ethereal oil; it is easily purified by solution in water, precipitation of the colouring matter by lead acetate, and recrystallisation from water. It then presents a well-defined crystallised form, requires 300 parts of cold water for solution, but is soluble in all proportions in hot water, alcohol, and glacial acetic acid; the crystals are insoluble in chloroform, ether, and benzene. Naringin melts in its water of crystallisation at 100°, losing 14 per cent. of its weight, whilst the anhydrous substance melts at 171°; it possesses a bitter taste, and has a specific rotation $[a]j = 64{\cdot}57$ (left).

Acids precipitate naringin from its solution in alkalis, but the precipitate is generally more or less yellow coloured, from the presence of a decomposition product, the amount of which depends on the duration of the action of the alkali; it appears almost impossible to free naringin from this colouring matter by repeated crystallisations, and in this respect it resembles hesperidin; lime water saturated when hot with naringin, solidifies on cooling to a jelly; acids easily decompose naringin when heated with it, producing, according to Dehn, "hesperidin sugar," and Dehn states that this sugar does not decompose alkaline copper solution completely, but the author cannot corroborate this statement. The empirical formula for naringin appears to be $C_{23}H_{26}O_{12} + 4H_2O$; from this substance hesperidin, limonin, and murrayin are easily distinguished by their melting-points, &c. Naringin when fused with potash, unlike hesperidin, does not yield protocatechuic acid; hesperidin and limonin melt at 245°, whereas murrayin (from *Murraya exotica*), melts at 170°. Murrayin is coloured blue-green by ferric chloride, and fluoresces blue, whereas naringin is coloured reddish-brown by ferric chloride, and does not fluoresce. E. W. P.

Lactucone. By N. Franchimont and Wigman (*Deut. Chem. Ges. Ber.*, **12**, 10—11).—Lactucone, $C_{14}H_{24}O$, is prepared by dissolving in boiling alcohol the residue which remains after repeatedly treating lactucarium (obtained from *Lactuca altissima*) with weak spirits of

wine. It forms microscopic crystals (m. p. 296°) which dissolve freely in petroleum, and sparingly in alcohol, but are insoluble in water.

By the action of phosphorus pentasulphide on lactucone, a hydrocarbon, $C_{14}H_{22}$, is obtained, boiling between 247° and 252°

W. C. W.

Betulin. By N. Franchimont and Wigman (*Deut. Chem. Ges. Ber.*, **12**, 7—10).—Betulin, $C_{36}H_{60}O_3$, extracted from birch bark by boiling alcohol, and purified by recrystallisation from petroleum and from benzene, forms colourless, needle-shaped crystals (m. p. 251°). By the action of phosphorus pentasulphide a hydrocarbon was obtained, boiling at 250—255°, and probably having the composition $C_{12}H_{18}$. Both the action of oxidising agents and attempts to obtain nitro-products, or sulpho-derivatives from this hydrocarbon, led to negative results. W. C. W.

Daphnetin. By C. Stünkel (*Deut. Chem. Ges. Ber.*, **12**, 109—115).—Rochleder has shown (*Ber. Wien. Akad.*, 1863) that daphnin and aesculin have the same composition, $C_{15}H_{16}O_9 + 2H_2O$, and that daphnetin and aesculetin, which are formed by the decomposition of these glucosides, both have the same rational formula, viz., $C_9H_6O_4 + H_2O$.

To prepare daphnetin, the alcoholic extract of the bark of the spurge laurel is heated with hydrochloric acid (a large excess of acid is to be avoided) and evaporated to dryness on a water-bath. The residue is exhausted with water, and daphnetin is separated from the solution by fractional precipitation with lead acetate; the first precipitate contains most of the impurities. The substance is obtained in a state of purity by decomposing the lead compound with sulphuretted hydrogen. Daphnetin crystallises in yellowish prisms, which are soluble in hot water and alcohol, also in concentrated sulphuric and hydrochloric acids, and in solutions of the alkalis and alkaline carbonates. The aqueous solution gives a yellow precipitate with lime-water, baryta-water, and lead acetate. It reduces silver nitrate and alkaline solutions of copper oxide.

Daphnetin melts at 253—256°, with partial decomposition.

Monacetyldaphnetin, $C_9H_5(C_2H_3O)O_4$ (m. p. 129—130°), forms long yellow prisms, soluble in ether, chloroform, benzene, and glacial acetic acid. By the action of an alcoholic solution of bromine on this compound, crystals of *tetrabromacetyldaphnetin*, $C_9HBr_4(C_2H_3O)O_4$, are produced. They melt at 290°, and are characterised by their insolubility in the usual solvents.

Benzoyldaphnetin, $C_9H_5(C_7H_5O)O_4$, crystallises in white needles (m. p. 150°) which are soluble in benzene, chloroform, and glacial acetic acid. Definite results were not obtained, either by the action of reducing or of oxidising agents on daphnetin. W. C. W.

Spergulin, a new Fluorescent Body. By C. O. Harz (*Chem. Centr.*, 1879, 24—30).—Spergulin occurs in the seed coverings of *Spergula vulgaris* and *S. maxima*. It is produced at the time when the seeds blacken and are nearly ripe. Spergulin is very soluble in absolute and aqueous alcohol. Viewed by transmitted light the solution appears nearly colourless, with a shade of olive-green; by reflected

light it exhibits an intense dark-blue fluorescence. Spergulin has not been obtained in the form of crystals. It is very soluble in methylic alcohol, less soluble in amylic alcohol, and scarcely soluble in petroleum or in ether. Concentrated sulphuric acid dissolves it, forming a dark-blue liquid. The fluorescence of an alcoholic solution of spergulin is maintained for more than a year if the liquid be kept in darkness; fluorescence is rapidly destroyed by the action of direct sunlight, and more slowly by that of diffused daylight.

Small quantities of caustic alkalis, or alkaline carbonates added to an alcoholic solution of spergulin, transform it into an emerald-green fluorescent body; basic lead acetate produces a precipitate in an alcoholic solution of spergulin. The new compound contains 61·85 per cent. of carbon, 7·05 of hydrogen, and 31·80 of oxygen, which agrees tolerably with the formula $C_5H_7O_2$. It appears to be related to chlorophyll, and is probably closely allied with phyllocyanin.

An alcoholic (1 : 8) solution of spergulin showed strong absorption, almost entirely in the violet; in this respect it differs considerably from chlorophyll, phyllocyanin, and phylloxanthin. The author is inclined to regard spergulin as a feeble acid, the acid salts of which, as well as the acid itself, exhibit blue fluorescence, the neutral salts exhibit green fluorescence, and the basic salts are without fluorescent properties. M. M. P. M.

The Colouring Matter of Sandal and Caliatour Woods. By N. Franchimont and Sicherer (*Deut. Chem. Ges. Ber.*, **12**, 14—17).—An amorphous substance having the composition $C_{17}H_{16}O_6$ is obtained by treating sandal wood with boiling alcohol, and precipitating the concentrated extract with water. The crude product is converted into the lead salt, which, after washing with hot alcohol, is decomposed by dilute sulphuric acid. A better yield of this colouring matter is obtained from caliatour wood than from sandal wood. The pure substance melts at 104—105°, and is soluble in alcohol, acetic acid, alkaline carbonates, and in caustic alkalis. It is precipitated from alkaline solutions by the addition of hydrochloric acid.

On fusion with potash, resorcinol, acetic acid, and probably pyrocatechol and protocatechuic acid are formed. On oxidation with potassium permanganate, oxalic and acetic acids are obtained, as also a substance resembling vanillin in odour. Reducing agents appear to have no action on this colouring matter. By the action of hydrochloric acid at 180° it is decomposed into (1) methyl chloride, (2) a body soluble in hydrochloric acid, which crystallises in colourless needles, and which forms a crystalline precipitate (m. p. 81°) with bromine-water, (3) a substance soluble in alcohol, having the composition $C_8H_{10}O_5$, and (4) a black residue insoluble in alcohol, but soluble in caustic alkalis. W. C. W.

Aspidospermine. By G. Fraude (*Deut. Chem. Ges. Ber.*, **11**, 2189—2191).—Aspidospermine is the alkaloïd which occurs in the bark of a tree growing in the neighbourhood of Catarmacca (Santiago), which has been styled *Aspidosperma quebracho* by Schlectendahl. This bark is used as a febrifuge, and in its action re-

sembles cinchona bark. The alkaloïd may be extracted from the bark by treatment with dilute sulphuric acid. The extract is then precipitated with lead acetate solution to remove tannic acid; the filtrate freed from lead by hydrogen sulphide, and the clear solution is then treated with solid sodium carbonate until it is alkaline, and the precipitate thus obtained after being dried is extracted with alcohol. On evaporation, the alcoholic extract yields the alkaloïd as a crystalline mass. This is further purified by boiling its alcoholic solution with animal charcoal, and several crystallisations from alcohol; the alkaloïd is thus obtained in white prismatic crystals, dissolving easily in alcohol and ether, but sparingly in water, and melting at 205—206°. It is decomposed when strongly heated, the vapours having an odour resembling that of acrolein. When fused with potash, vapours having the odour of pyridine and chinoline bases, are formed. Its hydrochloride and sulphate are both easily soluble in water; their solutions have an intensely bitter taste. The hydrochloride produces a white flocculent precipitate with mercuric chloride, and a white amorphous precipitate with phosphotungstic acid. The platinum salt is formed by adding a slight excess of platinum tetrachloride to a solution of the alkaloïd in hydrochloric acid; it is thus obtained as a crystalline precipitate. Its aqueous solution becomes coloured on standing, and in the presence of excess of platinum chloride becomes violet.

The analyses of the alkaloïd and of the platinum salt show the formula for the base to be either $C_{22}H_{30}N_2O_2$ or $C_{22}H_{28}N_2O_2$.

P. P. B.

Creatinine and Creatine. By T. Weyl (*Deut. Chem. Ges. Ber.*, **11**, 2175—2177).—When solutions of creatinine salts are heated with a dilute aqueous solution of sodium nitro-prusside, and a few drops of dilute caustic soda added, a beautiful ruby-red colour is produced. This reaction is characteristic for creatinine, and although very delicate the colour remains but a short time. It may be used to show the presence of creatinine in urine; the presence of sugar and albumin in the latter does not interfere with the delicacy of the reaction, but alcohol appears to render it less delicate. The presence of creatine in milk may also be demonstrated by means of this test, for although creatine itself does not exhibit this reaction, it may be easily converted into creatinine by boiling with dilute sulphuric acid. P. P. B.

Formation of Xanthine Derivatives from Albumin. By H. Krause and G. Salomon (*Deut. Chem. Ges. Ber.*, **12**, 95—96).—Blood fibrin, which has been exposed to putrefaction for 2—6 days, contains hypoxanthine. Hypoxanthine can also be obtained by digesting blood fibrin with very dilute hydrochloric acid (8 parts of acid to 1,000 of water) for one or more days. W. C. W.

Oxidation Products of Cinchonine. By W. Königs (*Deut. Chem. Ges. Ber.*, **12**, 97—101).—On oxidation with chromic acid, cinchonine yields an acid having the composition $C_{10}H_7NO_2$, perhaps chinoline-carbonic acid, $C_9H_6N.COOH$, which is identical with Weidel's cinchonic acid, $C_{20}H_{14}N_2O_4$ (*Annalen*, **173**, 76). On distillation with quicklime, this acid is decomposed into chinoline (b. p. 227—228°) and

a weaker base, $C_{12}H_9N$, which forms white needle-shaped crystals (m. p. 192°).

Oxycinchonic acid, $C_{20}H_{14}N_2O_6$, or *oxychinolinecarbonic acid*, $C_{10}H_7NO_3$, formed by fusing cinchonic acid with potash, crystallises in silky white needles, soluble in hot alcohol and acetic acid. The acid sublimes when carefully heated. The copper salt crystallises in pale-green needles; the silver salt dissolves in hot water, and is deposited from the solution on cooling in white plates. The barium, calcium, lead and mercury salts are soluble. By the action of phosphorus pentachloride, one OH group in the acid is replaced by chlorine.

By reduction with hydriodic acid, a feeble base is obtained, which appears to be identical with that produced by treating chinoline with zinc-dust. W. C. W.

Paraglobulin. By O. Hammarsten (*Pflüger's Archiv. f. Physiologie*, **17**, 413—468; and **18**, 38—116).—The author claims to have discovered in magnesic sulphate a reagent which is superior to all others for the detection of paraglobulin. When a solution containing nothing but paraglobulin is fully saturated with this salt, precipitation is absolute and complete within a short time: the presence of serum albumin slightly interferes with its action. Mainly by means of the sulphate, the author proves that the separation of paraglobulin from its solutions by the processes in ordinary use, viz., saturation with sodium chloride, treatment with carbonic acid, treatment with acetic acid and dilution, and dialysis, is never complete. Indeed, when sodium chloride is used, he shows that, in the case of horse-blood serum, as much as ·488 per cent. of paraglobulin may remain in solution, the quantity not precipitated varying with the temperature, &c. This to some extent bears out the statement of Heynsius, that by first treating serum with carbonic acid, and subsequently saturating with sodic chloride, more paraglobulin is obtained than by the latter operation alone.

The following is the author's process for estimating paraglobulin: 5 c.c. of the serum are mixed with 25 c.c. of saturated magnesic sulphate solution, and finely-powdered sulphate added in excess. The mixture is stirred occasionally for one or two days, and then filtered through a weighed filter. The precipitate is thoroughly washed with saturated magnesic sulphate solution, until the filtrate no longer becomes opalescent on addition of acetic acid and boiling. It is then heated at 110° C. for a few hours; after which it may be safely washed with boiling water, extracted with alcohol and ether, dried and weighed.

The author has satisfied himself that in this process serum-albumin is never precipitated with paraglobulin. Moreover, in an extended series of analyses, the paraglobulin determined by magnesic sulphate, and the albumin estimated in the filtrate in the usual way, were always equal to the total albuminous matter directly estimated. And he has shown, by the method of fractional precipitation, that the precipitate from blood-serum consists of paraglobulin alone, unmixed with any second substance.

Applying his method of analysis to the blood-serum of different

animals, he finds paraglobulin to be much more abundant than it is usually thought to be. This is shown by the following table of mean results :—

Blood, Serum of	Solid Matter.	Total Albumin.	Globulin.	Serum-albumin.	Lecithin, Fat, Salts, &c.	Ratio of Paraglobulin to Serum-albumin.
Horse	8·597	7·257	4·565	2·677	1·340	$\frac{1}{\cdot 591}$
Bullock ...	8·965	7·499	4·169	3·3299	1·466	$\frac{1}{\cdot 842}$
Man	9·2075	7·619	3·103	4·516	1·5876	$\frac{1}{1\cdot 511}$
Rabbit....	7·525	6·225	1·788	4·436	1·229	$\frac{1}{2\cdot 59}$

It follows, of course, that what has been hitherto regarded as serum-albumin, is in reality a mixture of that substance with paraglobulin.

Returning to the action of sodium chloride on paraglobulin, the author states that from a solution containing the least possible excess of alkali, it is precipitated by very minute quantities of sodium chloride; but that the precipitate re-dissolves on further addition of the salt, or on diluting. Paraglobulin is not precipitated from serum by the addition of 18—21 per cent. of salt. He agrees with Schmidt that paraglobulins from various sources, and variously prepared, are not equally soluble in weak salt solutions; but he has never succeeded, by repeated precipitations, in preparing paraglobulin completely insoluble in such solutions, as Schmidt claims to have done. He finds however that, when so treated, paraglobulin gradually becomes modified in such a way as to be rendered completely *precipitable* by solid sodic chloride, and finally to lose entirely its fibrino-plastic action on fibrinogen solutions. Hence he inclines to Brücke's view, that the partial solubility of paraglobulin in saturated salt solution depends on the presence of some third body, which, together with fibrin-ferment, is gradually separated from it by repeated precipitations.

The coagulating point of paraglobulin is usually stated to be 75°. The author finds, however, that it varies between 68° and 80°, being influenced by the method of preparation of the globulin, the strength of the solution, rapidity of heating, presence of salt, &c.

The fibrin-ferment being destroyed at a temperature of 58°, the author has succeeded in preparing paraglobulin free from it by heating its solution for a short time to that temperature. By this treatment also the coagulating point of paraglobulin is lowered, it becomes less soluble in weak salt solutions, and becomes fibrino-plastically inactive or nearly so. Here again the changes are probably due to the destruction of the ferment rather than to a modification of the paraglobulin.

Schmidt asserts that there exist certain liquids containing fibrinogen,

which are only coagulated by fibrin-ferment after the addition of paraglobulin: hence he concludes that these two globulins take part in the formation of fibrin. This theory the author controverts by showing that one of these so-called fibrinogenous liquids, the hydrocele secretion, actually contains a large quantity of paraglobulin, hitherto overlooked, which may be estimated at from ·366 to ·968 per cent. This paraglobulin also, when isolated, has not the slightest fibrino-plastic action. Schmidt's results are to be traced to the extreme dilution of his ferment solution.

Finally, the author has discovered a new method for preparing the fibrin-ferment in a concentrated state, and quite free from paraglobulin. This consists in saturating blood-serum with magnesic sulphate, and filtering off the paraglobulin. On cautiously adding alkali to the filtrate, a precipitate of magnesic hydrate falls, carrying with it the fibrin-ferment and some albumin. This is dissolved in dilute acetic acid, and the magnesic acetate removed by dialysis. The remaining solution possesses, sometimes to an extraordinary degree, the power of coagulating fibrinogen solutions without the addition of paraglobulin.

Fibrin is regarded by the author as the product of the mutual action of fibrinogen and the ferment alone.

Many other experiments are cited in these papers, principally in support of the conclusions given above. Ch. B.

Physiological Chemistry.

Researches on the Chemical Changes occurring in the Fowl's Egg during Incubation. By R. Pott (*Landw. Versuchs. Stat.*, **23**, 203—247).—The author made four experiments with 63 eggs in an incubator which he describes. Of the 63 eggs, 28 were hatched, and the most favourable time for hatching was found to be in May. The average weight of the eggs was 50 grams.

Loss of Weight of the Egg.—The author's observations show that this commences the day the egg is introduced into the incubator, and continues until the maturity of the embryo. At the end of the second day the egg has lost 2·82 per cent. of its weight; the loss from the 3rd to the 5th day is 1·82 per cent.; from the 6th to 7th day ·97 per cent.; from the 8th to 9th day 1·17 per cent.; from the 10th to the 11th day the loss rises to 2·02 per cent.; from the 12th to 13th day it is 2·49 per cent., and from the 14th to the 15th day 2·93 per cent. The author compares with this the loss of weight observed in an egg *that remained undeveloped at* 39° *C.* Its loss of weight increases from day to day, but more rapidly at the beginning of the third week than before. It attains its maximum at the end of the third week. No further diminution of any consequence takes place after this. The loss of weight in this egg and in that undergoing incubation at 39 C., is about the same during the first two weeks. In the third week, however, the latter suffers a greater loss of weight.

A new laid egg *exposed to the temperature of the air* also loses weight.

The loss of weight, however, is less than in the two foregoing cases, as a period of fifteen days is required before its loss equals that of the incubating egg on the second day.

Loss of Weight on Boiling.—Good eggs, the author found, lose on an average 0·26 per cent. of their weight, and rotten eggs 2·07 per cent. in weight.

Respiration of the Egg.—The author employed an apparatus by which the carbonic acid and water given off by the egg were estimated. The results show that the loss of weight of the egg undergoing incubation, of the non-developing, and of the fresh egg, consists essentially in an excretion of carbonic acid and water. The amount of water given off by the incubating egg is always greater than the amount of carbonic acid. In the egg remaining undeveloped at 39° C., the water is given off in considerably greater quantity than the carbonic acid. In this case the excretion is, of course, not due to respiration, but to the chemical decomposition of the constituents of the egg brought about by the warmth.

The Mechanical and Chemical Composition of the Egg.—The change in composition of the incubating egg can first be detected by the balance after 48 hours. The albumin of the egg first loses weight; the weight of the shell remaining almost unchanged throughout incubation. The loss of weight of the contents of the egg consists partly in a loss of dry substance, and partly in a loss of water. But what the internal parts of the egg lose the embryo gains in both substances. The greater part of the water is used externally in the process of respiration. In the egg remaining unincubated, a loss of weight of the contents also takes place, but entirely externally. The egg remaining unincubated, although kept for a considerable time at a temperature of 39° C., is distinguished from the fresh egg by its less weight, and from the incubated egg by the greater weight of its shell. The greater thickness of the shell, the author thinks, may be partly the cause of its non-incubation, by rendering more difficult the equable warming of the internal parts, and by its presenting greater resistance to the passages of gases in respiration. The greater weight of the shell is due simply to its containing a larger proportion of water.

The author finds, in opposition to what is usually stated, that the shell does not contribute to the development of the embryo until quite the end of incubation. The mineral components of the internal parts of the egg, on the contrary, diminish visibly with the process of incubation, and their diminution can only be attributed to an increase in the mineral components of the embryo. The components of the contents of the egg, which are soluble in ether, but especially those of the yolk, undergo a continual diminution during incubation; but as the embryo throughout incubation only contains small quantities of fat, they must be chiefly consumed in the respiratory process. The egg remaining undeveloped at 39° C. suffers very little change in its content of fat at first; subsequently the loss of fat is somewhat greater. The loss of nitrogen of the contents of the egg during incubation is proportional to the increase of that element in the embryo.

E. C. B.

Action of Cacodylic Acid on the Animal Organism. By H. Schulz (*Deut. Chem. Ges. Ber.*, **12**, 22—23).—Experiments on rabbits and on frogs show that cacodylic acid is poisonous. A subcutaneous injection of four decigrammes of the pure acid proved fatal to rabbits in the course of seven hours. W. C. W.

Action of Mono- and Di-phenylarsinic Acids on Animals. By H. Schulz (*Deut. Chem. Ges. Ber.*, **12**, 21—22).—A rabbit was killed by a dose of one decigramme of diphenylarsinic acid, administered by subcutaneous injection. A somewhat larger quantity of mono-phenylarsinic acid was required to produce the same effect. W. C. W.

Chemistry of Vegetable Physiology and Agriculture.

Researches on Beer Yeast. By P. Schützenberger and A. Destrem (*Compt. rend.*, **88**, 287—289).—Experiments undertaken to compare the chemical modifications experienced by yeast in presence of sugar with those which occur when it is left to itself under similar conditions, but without sugar, show that the quantities of oxygen absorbed, or of sugar decomposed in the unit of time, are proportional to the quantity of yeast employed, are functions of the temperatures, and are independent (within limits) of the quantities of oxygen and sugar present. In comparing two experiments made under different conditions, the time element must not be neglected, since during the longer interval the yeast may undergo modifications unconnected with the fermentation, which have not time to show themselves during a short experiment.

The present experiments were carried out with a sample of fresh Alsatian yeast.

First Series.—Yeast, 50 grams; water, 1,000 grams; white sugar, 100 grams.

Second Series.—Yeast, 50 grams; water, 1,000 grams. The two series of mixtures were placed in a stove at 33° C. for 24 hours, when all the sugar had disappeared. The liquids were boiled, filtered through tared filters, the residues washed with hot water, dried at 110°, and weighed; the filtrates distilled down in a vacuum, and the residues dried at 100° in a vacuum and weighed.

Referred to 100 parts of fresh yeast the results may be thus tabulated:—

	Fresh Yeast.			Second series.			First series.		
	Insoluble Residue.	Soluble Residue.	Total.	Insoluble Residue.	Soluble Residue.	Total.	Insoluble Residue.	Soluble Residue.	Total.
Ash	0·21	2·02	2·23	0·28	1·94	2·15	0·25	1·84	2·09
Carbon ..	10·60	3·16	13·76	9·18	2·86	12·04	9·27	7·75	17·02
Hydrogen	1·48	0·35	1·83	1·41	0·48	1·89	1·34	1·30	2·64
Nitrogen .	2·20	0·61	2·81	1·62	0·88	2·63	1·50	1·20	2·70
Oxygen ..	6·50	0·50	7·00	5·04	2·24	7·15	6·64	7·91	14·50
Total ..	20·99	6·64	27·63	17·53	8·40	25 86	19·00	20·00	38·95

The loss of solids amounting to 1·177 per cent. by simple digestion of the fresh yeast, is due to the secondary fermentation of the yeast itself observed by Pasteur. In the experiments with sugar there is an increase of solid matter equal to 11·3 per cent. of yeast, or 5·7 per cent. of sugar; this is due to the products of that portion of sugar which escapes fermentation, as Pasteur has shown. Admitting that the loss in the second series (= 1·77) also takes place in the first series, the gain due to the sugar will be 7·4 cent. of sugar.

The insoluble residue after fermentation contains less carbon and nitrogen than that of the fresh yeast, and as much oxygen: compared with the residue of the yeast digested without sugar, it contains about the same quantity of carbon, nitrogen, and hydrogen, but more oxygen. This difference is explained by the fact that the proteïd compounds in the simple yeast residues contain only 23 or 24 per cent. of oxygen, whilst the fermentation residue is partly made up of carbohydrates (derived from the sugar), which contain 50 per cent. of oxygen.

The proportion of albuminoïd matters transformed and eliminated is the same in the two cases, as is shown by the weight of nitrogen remaining constant: but in the simple digestion, some carbohydrate is destroyed, which either remains or is replaced in the fermentation.

J. M. H. M.

Composition of Beer Yeast. By P. Schützenberger and A. Destrem (*Compt. rend.*, **88**, 383—386).—According to Schlossberger, when yeast is treated with cold dilute potash lye, a solution of the albuminoïd matter is obtained, which may be precipitated by acetic acid, and a residue of cellulose is left. The composition of the albuminoïd precipitate, according to the authors, may be represented in its simplest form by the formula $C_{12}H_{21}N_3O_3$. The residue, however, does not possess the character of cellulose; it is insoluble in Schweitzer's reagent, and when treated with dilute sulphuric acid, it undergoes a decomposition similar to that of the glucosides under the same conditions. According to the analysis it contains, C, 54·79; H, 8·01; N, 5·43; O, 34·47. By treating this compound with a stronger solution of potash, a white flocculent amorphous body is obtained

of the formula $(C_9H_{16}O_5)_n$—a higher homologue of cellulose. The composition of the residue, insoluble in dilute potash, depends on the condition of the yeast from which it is obtained, as does also that of the final product, the cellulose; this may be seen from the following:—

	Percentage of insoluble matter.	Composition of insoluble matter.
Fresh yeast	19·5—20	$C_{18}H_{31}N_3O_8 = C_{12}H_{21}N_3O_3 + C_6H_{10}O_5$.
Yeast at 30° for 3 hours in presence of air....	18·6—19·5	$C_{18}H_{31}N_3O_8 = C_{12}H_{21}N_3O_3 + C_6H_{10}O_5$.
Yeast at 30° for 30 hours in atmosphere free from oxygen..	14·5—15	$C_{20}H_{33}N_3O_9 = C_{12}H_{21}N_3O_3 + C_8H_{12}O_6$.
Yeast fermented for 30 hours in twice its weight of sugar in atmosphere free from oxygen..	16·5—16·8	$C_{24}H_{41}N_3O_{13} = C_{12}H_{21}N_3O_3 + C_{12}H_{20}O_{10}$.
Yeast fermented as above in presence of air	25·1	$C_{22}H_{37}N_3O_{11} = C_{12}H_{21}N_3O_3 + C_{10}H_{16}O_3$.

The presence of oxygen does not affect the quantity or composition of the insoluble matter; when air is excluded, the quantity is increased, and the proportion of cellulose increased; this is due to decomposition taking place, whereby part of the proteïd goes into solution. Fermentation under similar circumstances produces the same effect, but with a greater assimilation of cellulose, which is still greater when the fermentation takes place in presence of oxygen.

The authors, therefore, consider yeast to contain a complex compound consisting of a proteïd and a cellulose, constituted similarly to the glucosides, and which like them may be decomposed by acids or alkalis, and moreover, the compositions of the two coats differ only by the interior coat containing a greater quantity of sugar.

L. T. O'S.

The Ferment produced by the Morbid Growth of the Bioplasm of the Yolk of Egg. By W. Thomson (*Analyst*, 1879, 9—10).—Under certain conditions a peculiar ferment is formed from the bioplasts of the yolk of an egg. This is a microscopic cell, and has been termed the "putrid cell," from its giving rise to a very putrid odour. The ferment first causes the yolk to swell considerably, and the white to become milky from the presence of the cells. Ultimately, the yolk becomes disintegrated and mixed with the white, and gas with offensive smell is produced. Similar cells have been detected in water in which putrid meat had been washed. The physiological effect of these ferment cells was tried by injecting albumin which contained them into the blood of a dog whilst under chloroform; the animal almost immediately had a slight convulsion and died. The

same dog had been put under chloroform before, and had perfectly recovered, but from a single experiment, the repetition of which would now be illegal, it would be rash to conclude that the chloroform had nothing to do with the fatal result. Should these putrid cells, however, be poisonous, their introduction into articles of food might afford an explanation of the hitherto inexplicable poisonous character of certain samples of food. F. C.

Distribution of Fungus. By E. Reichardt (*Arch. Pharm.* [3], **14**, 155—159).—Three cases are mentioned in which milk fermented, crystallisation of sugar from an alkaline solution ceased, and beer ferment ceased to act, in rooms which had been apparently thoroughly purified by whitewash, sulphurous acid, and chlorine. None of these disinfectants were, however, capable of completely destroying the fungus floating in the air, but it was found that fire had the desired effect. E. W. P.

On the Banana. By B. Corenwinder (*Compt. rend.*, **88**, 293—295).—Analyses made two or three years ago of bananas received from Brazil. The estimations were made on the edible portion of the fruit deprived of its rind.

Analysis of a ripe banana gave—

Water	72·450
Crystallisable sugar	15·900
Inverted sugar	5·000
Cellulose	0·380
Nitrogenous substances (0·342 N.)	2·137
Pectin	1·250
Fatty matter, organic acids, &c.	0·958
Inorganic matter	1·025
	100·000

Estimations of the sugars made day by day until rottenness began to set in, gave the following results:—

Condition of the fruit.	Crystallisable sugar.	Uncrystallisable sugar.	Total.
1. Ripe, sound, flesh still firm	15·90	5·90	21·80
2. „ „	15·72	6·34	22·06
3. „ „	15·10	6·43	21·53
4. „ „	14·28	6·69	20·97
5. Riper, flesh soft	12·25	8·95	21·20
6. Very ripe, flesh soft	10·16	8·92	19·08
7. „ „	9·26	9·75	19·01
8. „ flesh "sleepy" (blette)	4·51	11·70	16·21
9. „ „ „	3·13	12·90	16·03
10. „ flesh very sleepy	2·84	11·84	14·68

In the sound and ripe fruit, the total sugar may thus reach 22·06 per cent., and, as might be expected the proportion of inverted sugar

increases with the progress of the ripening. H. Buignet has previously found that during the period of growth, cane-sugar is the only sugar present. The nitrogen (0·342 per cent.) found in these bananas is equivalent to 1·242 per cent. of matter dried at 100°; in a banana from an unknown source, the author found N = 0·9 per cent., and in small bananas from Algiers, N = 0·614 per cent. of dried matter.

The author considers that the banana might be utilised to produce an excellent alcoholic spirit, and suggests the admixture of its juice with diluted molasses for fermentation in warm countries, as the juice of the beetroot is used with molasses in France. J. M. H. M.

Analytical Chemistry.

Quantitative Determination of Precipitates without Filtering, Washing, and Drying them. By R. Popper (*Zeits. Anal. Chem.*, 1879, 14—38).—This is the continuation and conclusion of a previous paper by the same author (*Chem. Soc. J.* [2], 1877, 638). The author in the present communication explains a more simple method of determining the sp. gr. of precipitates, and gives results obtained by the method when applied to some generally occurring precipitates. The formula employed is derived from that already given (*loc. cit.*), and the letters represent the quantities there stated. It is the following:—

$$S = \frac{N-(G-g)}{N}.s.$$

The sp. gr. (S) of the precipitate is determined by precipitating from the solution of a weighed quantity of a pure salt a known weight (N) of the precipitate. This avoids the inconvenience and loss of time incurred in washing the precipitate, and further gives its sp. gr. under the usual conditions of its formation.

Ferric Hydrate.—The method is useful for correcting the weight of a precipitate of aluminium hydrate when mixed, as is often the case, with a small known quantity of iron as ferric hydrate. The sp. gr. of the ferric hydrate precipitate was obtained by using known weights of Mohr's salt of ascertained purity. The mean of four fairly concordant results gave S = 2·72. These results varied more widely than usual, probably on account of the apparently capricious differences in the state of hydration of this precipitate.

Barium Sulphate.—For this precipitate, the mean of four very concordant results gave S = 4·525, and this number closely agrees with results published by Rose.

Mercuric Sulphide.—S = 7·346, a very satisfactory mean. This was considered the most useful precipitate for estimation of mercury, because in solutions sufficiently diluted, small quantities of nitric acid, ferric chloride, and even *aqua regia* had no bad influence, especially when the process was quickly carried out.

Nickel Hydrate.—The mean of three determinations gave S = 4·36.

Lead Sulphate.—Lead is most readily separated as sulphate from most of the metals associated with it in ores. In applying this method, excess of sulphuric acid must be added, and the coefficient of expansion of the dilute acid is slightly different from that of water, and varies also with the strength of the acid. In precise experiments the author used 1 vol. of acid to 40 of water. This acid has a coefficient of expansion of 11 compared with pure water as 8. For ordinary purposes this difference may be neglected, as the error incurred is not higher than 0·1—0·2 per cent. As a mean of four experiments, S = 6·380.

The method was tested further by applying it to the estimation of mercury, aluminium, and sulphuric acid, in a mixture in known proportions of mercuric chloride, ferrous sulphate, and potash alum. After dissolving the substance in water and acidifying with hydrochloric acid, the mercury was precipitated with sulphuretted hydrogen, and liquid and precipitate made up to a litre in a litre flask. When the mercuric sulphide had settled, a portion of the liquid was syphoned off through a filter, as described in the former paper (*loc. cit.*), and its sp. gr. determined. The sp. gr. bottle was then filled with this liquid and the precipitate weighed. The mercury found was 30·67 per cent., against 30·75 put into the mixture. Two portions of 400 c.c. each of the decantate were then boiled until free from sulphuretted hydrogen. In one the iron was determined by permanganate; the other was precipitated by ammonia after oxidising the iron with nitric acid. The weight of the precipitate of ferric and aluminium hydrate was determined by the author's method: allowing for the known quantity of iron, the weight of aluminium was found. The weights found were aluminium 2·45 per cent., iron 3·39, against 2·41 and 3·36 respectively put into the mixture. The sulphuric acid found in the liquid decanted from the precipitate with ammonia was 23·02 per cent. by this method, against 23·086 actually present. The method is suggested for estimating impurities remaining as residues, such as barium sulphate left from adulterated zinc-white when treated with hydrochloric acid; also for the estimation of cadmium sulphide left undissolved when cadmium and tin sulphides have been treated with ammonium sulphide. The author is satisfied that the sp. gr. of a precipitate may be considered invariable, except in cases like calcium carbonate, when the precipitate may exist in two modifications.

In conclusion the author gives numerous precautions to be observed. Amongst them are the following. The liquid above the precipitate, unless already mixed by boiling or the passage of a gas, must be vigorously stirred to render it homogeneous. Large quantities of dissolved substances should be avoided, as they affect the coefficient of expansion. The precipitate and liquid should be weighed before the liquid alone, as the small quantity of the former liquid is more rapidly affected by evaporation than the latter; and both weighings should be made as rapidly as possible to avoid difference of temperature. The temperature should be read to the tenth of a degree, and the ordinary precautions taken to avoid errors by heating with the hand or neighbouring flames after reading the temperature. When such

obviously requisite precautions are attended to, the results are uniformly satisfactory. F. C.

Determination of Phosphoric Acid as Phospho-molybdate. By O. Hehner (*Analyst*, 1879, 23—31).—The author reviews all that has previously been contributed towards the estimation of phosphoric acid, either directly as phospho-molybdate, or indirectly by dissolving this precipitate in ammonia, precipitating with magnesia mixture, and weighing as magnesium pyrophosphate. The objection to weighing the dried phospho-molybdate precipitate is that it has been found to contain percentages of phosphoric anhydride varying from 3·14 to 3·90. The explanation given by Lipowitz, that this variation is due to MoO_3 accompanying the precipitate in varying proportions, is confirmed by the author, who found further that the quantity of MoO_3 precipitated increased with the temperature at which the precipitation took place. Hence low temperatures (30—35° C.) should be employed. The molybdic solution is best prepared according to the directions of Fresenius, by dissolving 1 part of molybdic acid in 4 parts of ammonia of 0·96 sp. gr., and pouring this solution slowly into 15 parts of nitric acid of 1·2 sp. gr., avoiding all rise of temperature. When the precipitate was thrown down by means of the above molybdate solution in a solution previously nearly neutralised by addition of ammonia, and at a low temperature, it was found to be free from molybdic acid. It was soluble in 21,186 parts of water, in 8,117 of strong alcohol, and in 13,513 of dilute alcohol; hence this precipitate may be washed with dilute alcohol without sensible loss, and this is to be preferred to water, because it does not cause the precipitate to pass through a good filter. Direct experiment showed that no one of these three liquids dissolved the precipitate sensibly when used for washing.

The method finally adopted for getting the precipitate in a form suited for weighing was as follows. The phosphate was precipitated with the precautions already mentioned, and also avoiding too great concentration of the solution, which encourages the simultaneous precipitation of molybdic acid. This precipitate was washed with dilute alcohol, leaving as much of the precipitate as was possible in the beaker, the precipitate was dissolved from the beaker and filter by ammonia solution, and this solution was then evaporated to dryness on the water-bath, the evaporation to dryness being several times repeated after the successive addition of small quantities of water. The precipitate then consisted of ammonium phosphate and acid ammonium molybdate. It can be dried at 100° and weighed, a constant weight being quickly obtained, since all ammonia which ordinarily escapes during the drying process has been removed by the repeated evaporations. The weight of this precipitate when divided by 28·5 gives the weight of phosphoric anhydride present. Comparative results obtained by this method and by weighing as magnesium pyrophosphate were closely concordant. The precipitation requires only two or three hours, and the estimation may be easily completed in a day. To recover the molybdic acid from the residues, the author acidifies with nitric acid, adds sodium phosphate, dissolves the precipitate formed on heating in ammonia, preci-

pitates the phosphate with magnesia mixture, and the molybdic acid from the filtrate by nitric acid; the molybdic acid is filtered, washed, and dried. F. C.

Note on the Detection of Alum in Flour by the Logwood Test. By W. C. Young (*Analyst*, 1879, 6—7).—Logwood solution seldom fails to detect an adulteration of alum in bread, but as usually applied to flour has failed to detect alum when purposely mixed with the flour beforehand. The author finds that this is due to the alum not being in solution in the case of flour; but by mixing the flour into a paste with boiling water before adding the ammoniacal logwood tincture, he found that a bluish-grey colour appeared in a few minutes and remained for seven days, when only 5 grains of alum were present in 4 lbs. of flour. The fault may sometimes lie with the logwood infusion. This is always suitable for the test if it yields a deep claret colour on addition of solution of ammonium carbonate. F. C.

The Logwood Test for Alum. By W. Stoddart (*Analyst*, 1879, 7).—According to the author's experience, the test is quite reliable if the bread after treatment with infusion of logwood is exposed to the air for an hour or two. In the absence of alum, the purple colour changes to brown; if alum is present, it is permanently blue. The logwood must be freshly cut and kept in a closed bottle, and the alcoholic tincture or the decoction must be freshly prepared, otherwise the solution does not alter in colour on addition of an alkali, and is useless. F. C.

Detection and Estimation of Alum in Wheat Flour. By A. Dupré (*Analyst*, 1879, 1—5).—Flour may be tested for alum by the logwood test; if no result is obtained, alum may be considered to be absent: if alum is indicated by the logwood, its presence should be confirmed and its quantity estimated by other means. A ready method consists in shaking the flour with chloroform in a stoppered separating funnel and allowing the mineral residue to settle; the flour rises to the surface, and by opening the tap the mineral residue is obtained with a little chloroform. In estimating the amount of alum, the chloroform and flour must be repeatedly agitated without disturbing the residue, this is separated, and the agitation repeated as long as anything more settles: 100 grams of flour may be used, and from 300 to 500 c.c. of methylated chloroform. On extracting this mineral matter with water, the solution will be acid, and yield a precipitate with barium chloride solution, if alum has been added to the flour: ammonia is also readily detected if ammonia alum is present, but the alumina, which apparently remains in the flour which is in the deposit, must be extracted by boiling some of the deposit with very dilute hydrochloric acid. To estimate the quantity of alum present, the author recommends a careful determination of the sulphuric acid in the aqueous extract of the deposit, and calculation of the weight of alum corresponding to the weight thus found: the results yielded by flour adul-

terated with known proportions of alum were very satisfactory when thus estimated.

The author finds the deposit from chloroform well suited for examination by logwood, but the following precaution must be borne in mind. The soil and clay mixed with the flour give a blue colour with logwood; it is, however, somewhat darker, and less blue: if the clay be allowed to dry, its colour changes to pale grey with a tinge of red, whereas the alum and logwood retains its blue colour on drying. Hence, the colour must be judged only after drying, if logwood is employed.

Analyses of pure wheaten flour have been undertaken to ascertain whether the proportion between the silica and alumina found would not serve as a means for detecting the admixture of alum. The author found that this proportion was variable, whilst the quantities of silica and of alumina in different samples were very different. The following rule is, however, approximately true; flour containing from 0—5 grains of silica in 4 lbs. should not yield more alumina than is obtained by multiplying the weight of silica by 2·86: in flours containing from 5 to 10 grains, and from 10—15, the multipliers are 1·90 and 1·26 respectively. The possible error incurred is 6 grains in excess or defect, but this error represents a quantity of alum not injurious. This method will be found most useful in conjunction with the logwood test for testing bread; the method described above can be substituted for it in testing flour. F. C.

Estimation of Ferrous Oxide in Silicates. By C. Doelter (*Zeits. Anal. Chem.*, 1879, 50—58).—The method of fusing with borax proposed by Hermann almost always yields too much ferrous oxide, owing to reduction of some of the ferric oxide. If the silicate is dissolved by heating it with sulphuric and hydrofluoric acids in sealed tubes, the titration with permanganate gives too much ferrous oxide. This is due to the presence of sulphurous anhydride and sulphuretted hydrogen in commercial hydrofluoric acid. These impurities can be removed by distilling the hydrofluoric acid with permanganate, but for this, a platinum retort and receiver are indispensable. The author attempted to remove the error caused by these impurities by adding the requisite quantity of permanganate to the hydrofluoric acid before using it; the results were unsatisfactory. The method finally adopted was to evaporate the hydrofluoric acid entirely before titrating, and thus remove the impurities. The silicate is dissolved in a mixture of sulphuric and hydrofluoric acids in a platinum crucible placed on an iron plate which is heated beneath: the crucible is kept covered with an inverted beaker, into which a stream of carbonic anhydride is constantly passed by a tube entering through a hole in the top. The error was by this means rendered insignificant, and the possession of expensive platinum apparatus became quite unnecessary. F. C.

Estimation of Lead as Lead Iodate. By C. A. Cameron (*Analyst*, 1878, 338).—Lead iodate is far more insoluble than the sulphate, and if precipitated from solutions free from dissolved salts, it may be considered as absolutely insoluble. The gravimetric or volu-

metric method may be used; if the latter, the sodium iodate solution must first be standardised by a solution of pure lead nitrate, and after complete precipitation of the lead as iodate, the excess of sodium iodate in the filtrate and washings is determined by the hydrochloric acid and sodium thiosulphate method. F. C.

Analysis of Alloys containing Copper, Zinc, and Nickel. By T. Bayley (*Phil. Mag.* [5], **6**, 14—19).—The alloy is dissolved in nitric acid, and the solution evaporated to dryness with excess of sulphuric acid to expel the nitric acid, which must not be left in the solution.

Excess of potassium iodide having been added, the solution is titrated with sodium thiosulphate, every two grams of free iodine thus measured representing one gram of copper. The results of determinations of copper made by this method seem to show that when zinc or nickel is present, the numbers obtained are too low, thus in one case instead of ·2816 gram of iodine, the titration gave only ·2755.

The determination of the nickel is based on the fact that the colours of nickel and cobalt salts are complementary. If a solution of nickel be added gradually from a burette to a given quantity of cobalt solution, it is found that a colourless mixture is obtained when the amount of nickel present is from 3·1 to 3·2 times that of the cobalt. The addition of perfectly neutral ammonium carbonate greatly increases the delicacy of the test, the colour being purple when too little nickel is present, and blue when there is too much. By this means the colour coefficient of nickel with regard to cobalt was found to be 3·16, a number on which the nature of the salts employed has no influence.

The actual method of proceeding is as follows: standard solutions of cobalt and nickel salts are prepared, as also a solution of neutral ammonium carbonate containing 26·5 grams of ammonia per litre. Three cylinders similar to those used for Nessler's test are then taken, and into each a quantity of the cobalt solution is placed, containing ·0078125 gram of the metal; to the first ·024531 gram of nickel in solution is added, to the third ·0248458 gram. 25 c.c. of the ammonium carbonate solution is poured into each of the three cylinders, which are then filled up with water to 150 c.c.; the first has now a purple, the third a blue tinge. The solution containing the nickel to be estimated is now added to the second cylinder until the colour is between the other two.

After the determination of the copper and nickel by the above methods, the zinc is obtained by difference. F. D. B.

The Inconstant Composition of Well Waters. By C. A. Cameron (*Analyst*, 1878, 337).—The water taken from a deep well on two different occasions showed a remarkable difference in character and purity according as it was taken from the surface by dipping, or was pumped from near the bottom at a depth of over fifty feet. The surface water of the well was yellowish in colour, and was much harder and much more contaminated with organic impurities than that from the bottom of the well. It was evident that a layer of somewhat lighter water derived from surface drainage floated on the effi-

ciently filtered spring water which was supplied to the lower part of the well. The author has noticed a similar difference in quality of the water drawn at different depths from four other wells: in one case the solids per gallon amounting to 66·23 grains in the bottom water and to only 3 grains in the surface water: such variations are not, however, always observable in deep well waters. F. C.

Nitrogen Compounds present in Cereals. By G. W. Wigner (*Analyst*, 1878, 358—362).—The nitrogen determinations given in a previous paper (this Journal, **34**, 1014) were made by the soda-lime process. The author now finds that the results yielded by combustion with soda lime are not concordant with those yielded by Dumas' method: the results yielded by the nitrogenous substances coagulated by washing with carbolic acid are more correct, and the non-coagulable substances apparently interfere with the accuracy of the results when the soda-lime process is used.

In some cases the nitrogen in whole meal equals the sum of that found in bran and in flour, but in many cases this is not found to be so. A determination of nitrogen present as nitrates and nitrites proves that in bran, an average of 0·39 per cent., and in flour of 0·13 per cent. of nitrogen is present not as true gluten or as a nitrogen acid: the author suspects the presence of a body of the asparagine class. Probably only the coagulated nitrogenous substances must be accounted to be flesh-formers. Of these, whole meal contains an average of 8·09 per cent., and flour of 8·33 per cent., showing a difference of 0·24 per cent. in favour of the flour. F. C.

Titration of Hydrocyanic Acid and Cyanides, and its Relation to Alkalimetry. By L. Siebold (*Analyst*, 1878, 343—347).—To insure accuracy when titrating hydrocyanic acid with decinormal silver nitrate solution according to Liebig's method, the hydrocyanic acid should be run into the solution of caustic alkali from a pipette dipped beneath the surface of the liquid, loss of acid is thus avoided; the acid should be diluted with from ten to twenty volumes of water, to render the final reaction more evident, and the quantity of alkali used must be slightly in excess of that required for forming an alkaline cyanide. If the caustic alkali is in large excess, the results are too high; if it is deficient, the results are too low, since only that portion of acid which has been converted into alkaline cyanide is estimated by the silver solution.

When the precipitate just becomes permanent, if the reaction of the liquid to test-paper is alkaline, it will indicate that an excess of alkali has been employed, but since the alkaline cyanides are themselves alkaline to test-paper, it is impossible to test before addition of silver nitrate. The addition of more alkali and continuation of the titration if insufficient alkali was added at first is inadmissible, since hydrocyanic acid at first left free would certainly have been partially lost during the first titration. The author obviates this difficulty, by running a known quantity of the hydrocyanic acid into an excess of sodium hydrate solution, then adding decinormal silver nitrate solution until a slight turbidity remains, and finally estimating the excess

of alkali by running in normal hydrochloric or sulphuric acid until the turbidity begins to increase, since this occurs only when the free alkali is exactly neutralised. For each c.c. of acid thus required, 0·01 c.c. should be deducted from the volume of silver solution used, and the remainder calculated into hydrocyanic acid.

Since silver nitrate only estimates the alkaline cyanide and not free hydrocyanic acid, the proportion of alkaline cyanide may be thus estimated in a solution which also contains hydrocyanic acid: in another portion of the solution which has been added to excess of sodium hydrate solution, the total cyanide may then be estimated as directed above, and the alkaline cyanide formed from the hydrocyanic acid found by difference. Hannay's method is extremely convenient and accurate for the estimation of cyanides, but fails to determine their proportion in a liquid which also contains free hydrocyanic acid. The author further proposes the use of this method for titrating free alkalis and alkaline carbonates: these when added to excess of hydrocyanic acid may be titrated with great precision by means of the silver nitrate solution and with the following advantages over the usual process of titration with standard acid, using test-papers as indicators. The solution of alkaline carbonate does not require to be boiled, as the carbonic acid does not interfere: the turbidity is more striking as a final reaction than the change of colour of the test-paper; the *decinormal* silver solution yields more accurate results than the *normal* acid solution. About 0·5—1 gram of the carbonate dissolved in 100 c.c. of water is mixed with 10—20 c.c. of Scheele's acid; each c.c. of silver solution added corresponds to 0·138 gram of potassium carbonate and to 0·0106 of sodium carbonate. If after titrating, the liquid is boiled until all free hydrocyanic acid is expelled, and a few drops of potassium chromate are added, titration again with the silver solution until a red colour appears will check the above titration, or if chlorides are present, the excess corresponds to the quantity of the chlorides: estimations of known quantities of carbonates and chlorides yielded almost theoretical results. F. C.

Estimation of Methyl Alcohol in Wood-spirit. By C. Bardy and L. Bordet (*Compt. rend.*, **88**, 236—239).—This method is in principle the same as that already proposed (*Ber.*, **6**, 1316), namely, the conversion of the methyl alcohol into moniodomethane, but differs from it in the method of procedure.

The apparatus used, of which a diagram is given, consists of a Liebig's condenser, on the inner tube of which three bulbs are blown, which are surrounded by the outer tube. The inner tube is connected with a small flask into the neck of which a small pipette, fitted with a stop-cock and graduated to hold 5 c.c.. is ground so as to form a stopper.

The condenser is placed in a reversed position and 15 grams phosphorus iodide are placed in the flask, and, by means of the pipette, first 5 c.c. of wood-spirit are added slowly, drop by drop, and then the same volume of hydriodic acid, sp. gr. 1·7, containing in solution its own weight of iodine. The flask is then heated in a water-bath between 80° and 90° for a few minutes, afterwards the condenser is

placed in its ordinary position, and the contents of the flasks distilled into a graduated tube which is fixed into the other end of the condenser by means of a caoutchouc cork. When the distillation is finished, the distillate is shaken with water, and the volume of methyl iodide read off, corrections being made for its solubility in water (8 per 1,000) and also for the volume of methyl iodide which, in the state of vapour, fills the apparatus. The latter, which always remains the same for the same apparatus, is determined by distilling a given volume of methyl iodide in the apparatus, measuring the distillate and noting the difference in volume, which is equal to the amount of methyl iodide remaining in the state of vapour.

When acetone is present, it distils over, and it is only with very constant washing with water that the distillate can be freed from all traces of it. The authors have determined the diminution in volume which methyl iodide containing from 10 to 30 per cent. of acetone undergoes when washed with water, and have constructed a table, so that to eliminate the error arising from the presence of acetone after shaking the distillate with water, the volume of CH_3I is noted, the water syphoned off, and the residue washed again with a volume of water equal to that of the methyl iodide; the diminution in volume of the methyl iodide is noted, and on reference to the table, the percentage of acetone may be ascertained.

From the results obtained, the method would appear to be trustworthy. L. T. O'S.

Detection and Estimation of Salicylic Acid in Animal Secretions. By P. Cazeneuve (*J. Pharm. Chim.* [4], **29**, 221—222). A more practical method than that of Yvon for the detection and estimation of small traces of salicylic acid in beverages or secretions of the body is the following:—100 c.c. of the liquid are evaporated to occupy 10 c.c., and, after the addition of 1 c.c. hydrochloric acid and 20 grams plaster of Paris evaporated to dryness on a water-bath. The residue is digested with chloroform which, in the case of urine, is mixed with ether. The chloroform is distilled, the residue dissolved in boiling water, and the solution filtered. If the quantity of salicylic acid be sufficiently large, it crystallises from the solution, and may be weighed, but if the solution is too dilute, it may be detected by the addition of a drop of ferric chloride. L. T. O'S.

Determination of Quinine in certain of its Salts. By B. W. Dwars (*Arch. Pharm.* [3], **14**, 149—155).—If a solution of a quinine salt be decomposed by a slight excess of ammonia, then shaken up with chloroform, and an aliquot portion of the chloroform be evaporated, the weight of the residue bears the same proportion to the total quinine as the two volumes of chloroform do to one another. As the temperature at which quinine sulphate gave up its crystalline water (7 mols.) appeared to be uncertain, the author has ascertained by experiment that at 100° the salt was completely dried, losing 12·8 per cent. H_2O. It was also ascertained that quinine dried at 100° was anhydrous. Ether cannot be substituted for chloroform because of its greater solubility in water. E. W. P.

Solubility of Cinchonine, and Estimation of Cinchona-barks. By L. Prunier (*J. Pharm. Chim.* [4], **29**, 135—139).—The solubility of cinchonine in various solvents has been determined by different chemists, but the results are far from concordant; the author therefore has determined its solubility in alcohol of 95 per cent., chloroform of normal density, and amyl alcohol, and finds that 1 gram cinchonine is dissolved by—

Alcohol 95 per cent.	Chloroform.	Amyl alcohol.
84·28	101·62	108·6

The solubility of the alkaloïd is increased by mixing these solvents in certain proportions, it being most soluble in a mixture of 4 parts of chloroform to 1 of alcohol, 95 per cent. The results are as follows:—1 gram of cinchonine is dissolved by—

45	grams of a mixture of	1	chloroform and	4	alcohol 95	per	cent.
21	„	„	1	„	1	„	„
43·47	„	„	4	„	1	„	„
13·27	„	„	6	„	1	„	„
27·24	„	„	1	„	1	amyl alcohol	
22·70	„	„	4	„	1	„	

The author has applied the solubility of cinchonine in a mixture of 4 chloroform to 1 alcohol to determine the total quantity of alkaloïds in grey Java cinchona-bark, and obtains better results than those obtained by Carle's method, or Chevalier and Baudrimont's method (*Dict. de Fabrication*, 5th edition, 918, note), which consists in exhausting the bark with a solvent not miscible with water (in this case a mixture of amyl alcohol and chloroform), and afterwards exhausting the solvent of the alkaloïd by shaking with hydrochloric or sulphuric acid. The results obtained are (1) by using a mixture of chloroform and alcohol (4 to 1) 4·3 per cent. of alkaloïd of the total weight of bark; (2) Carle's method, 4·0 per cent.; (3) Chevalier and Baudrimont's method (*a*) when shaken with HCl, 3·2 per cent.; (*b*) when shaken with H_2SO_4, 3·0 per cent. The loss in the two last results appears to be due to the solubility of the acids in chloroform.

The method adopted by the author for the estimation of alkaloïds in the bark is as follows:—10 grams of slaked lime are mixed with 300 grams of water and 20 grams of the finely powdered bark; the dry mixture is then exhausted with a mixture of chloroform and alcohol (4 to 1); water is added and the chloroform separated and distilled; the residue is dissolved in hydrochloric acid, and the free alkaloïds precipitated by addition of ammonia. The precipitate is collected and weighed after washing with ammonia. To separate the quinine from the cinchonine the weighed precipitate is exhausted with ether which leaves the cinchonine undissolved. Another method for the separation of the cinchonine is to precipitate the acid solution by sodium bicarbonate in presence of tartaric acid, when the quinine remains in solution. L. T. O'S.

Alkali-albuminate and Syntonin. By K. A. H. Mörner (*Plüger's Archiv. f. Physiologie*, **17**, 468—547).—This paper contains

an exhaustive and minute study of the behaviour of alkali-albuminate and the different modifications of syntonin with various reagents.

Ch. B.

Amount of Solids in Milk. By C. A. Cameron (*Analyst*, 1879, 11).—The results obtained in estimating the total solids present in twenty-six different samples of milk from Drogheda are stated and compared. The average percentage was 13·31, the minimum 12·19, and maximum 14·79; more than one-half of the samples contained over 13 per cent. of solids. These samples are believed to have been unadulterated. F. C.

Technical Chemistry.

Process for Enriching Phosphates containing Earthy Carbonates. By L. L'Hote (*Compt. rend.*, **88**, 295—296).—The phosphorites used in the south of France for the manufacture of superphosphate, contain about 70 per cent. phosphate of lime and 12 per cent. carbonate of lime. With these are found large masses containing too little phosphate and too much carbonate to be advantageously treated without concentration. The carbonate cannot be separated by mechanical means, and the chemical methods hitherto employed proceed by dissolving both the carbonate and phosphate in order to prepare a product similar to that known as *precipitated bone phosphate*.

At a red heat, these minerals lose only a part of their carbonic anhydride, but the author has found that by calcining them in a current of steam, the whole of the CO_2 may be expelled, and a friable mass obtained from which the quicklime may be easily removed by treatment with hydrochloric acid of 1° B. added in just sufficient quantity. The phosphate of lime rapidly settles, and after the removal of the calcium chloride by repeated washings, is ready for transformation into superphosphate. By this treatment poor phosphorites containing 36·28 per cent. and 38·52 per cent. of calcium phosphate, with 34·77 per cent. and 32·27 per cent. of calcium carbonate, were converted into products containing 75·69 per cent. and 80·47 per cent. of calcium phosphate respectively, with no carbonate. J. M. H. M.

Preparation of Alumina. By G. and F. Löwig (*Chem. Centr.*, 1879, 31).—A concentrated aqueous solution of potassium or sodium aluminate (see next abstract) is heated with milk of lime; a precipitate separates, containing 3 equivs. of lime to 1 of alumina. The supernatant liquid contains caustic alkali, which may be recovered by evaporation. The washed precipitate is divided into two equal portions, one of which is dissolved in hydrochloric acid, while the other is made into a milk with water, and is then slowly added to the solution in acid, until, on filtration, only traces of aluminium can be detected in solution. A precipitate of alumina is thus obtained, which is soluble in acetic acid, and is admirably adapted for decolorising sugar syrups and other coloured liquids. M. M. P. M.

Preparation of Alkaline Aluminates. By G. and F. Löwig (*Chem. Centr.*, 1879, 31).—In order to prevent formation of alkaline sulphates or nitrates, the alumina used should be fused with alkaline carbonate in the proportion of equal equivalents of each. If cryolite be used, it is necessary to mix it with two equivalents of alumina inasmuch as it already contains 3 equivs. of soda for 1 of alumina. If bauxite be employed the amount of alkali present as silicate should be determined, and an equivalent amount of lime should be added; alkaline carbonate should also be employed in amount equivalent to both the ferric oxide and alumina present in the material. The residue remaining after removal of the alkaline aluminate may be again fused with alkaline carbonate whereby caustic alkali is obtained.

Bauxite may also be decomposed by fusion with alkaline earths, or the carbonates of these earths; a portion of the alkaline earth decomposes the silicate of aluminium, whilst another portion combines with the alumina so set free to form an aluminate. M. M. P. M.

Solubility of Lime in Water in reference to the prescription for Aqua Phagedænica. By L. C. W. Cocx (*Arch. Pharm.* [3], **14**, 145—149).—It appears that none of the European pharmacopœias, except that of the Netherlands, states the correct amount of lime-water to be added to corrosive sublimate in the proportion, $HgCl_2 + Ca(HO)_2 = HgO + CaCl_2 + H_2O$, so as to produce the preparation *Aqua phagedænica*. This appears to be due to the uncertainty existing concerning the solubility of lime in water, which Lamy has shown, depends upon the method whereby the lime was produced, and the temperature at the time when the solution was prepared.

E. W. P.

Recovery of Antimony. By C. A. Hering (*Dingl. polyt. J.*, **230**, 253—263).—This article consists for the most part of the description of an attempt to obtain metallic antimony out of the refuse from the ordinary fusion process to which the sulphide of antimony is subjected, and of suggestions as to other methods. In the fusion process to obtain *Antimonium crudum* there is a large amount of the sulphide left in the refuse, especially when the temperature is kept rather low in order to obtain a fine clean-looking product.

When a piece of the refuse is broken, it is found to be studded with little fragments of antimony sulphide, whilst a thin coating of the same material covers the lump.

Many attempts have been made to recover this antimony, but without any practical result. The proposal of Lampadius to work up the fusion-refuse with a flux of Glauber's salt in the blast furnace appears to have remained quite unnoticed.

From the author's attempts to utilise the refuse, the precipitation process seemed to be the only one promising practical results. The average result showed that the refuse contained along with silica, alumina, lime, and sulphides of iron, &c., 20·4 per cent. of antimony sulphide, a quantity equivalent to 14·64 per cent. of metallic antimony.

A preliminary trial was made on a small scale in a wind furnace.

The charge—which was meant to be analogous to what would be required in working on a large scale—consisted of—

Fusion refuse	5	kilograms.
Puddling slag.....	3	„
Soda.....	2	„
Powdered wood charcoal	25	„

The product was 0·56 kilo. of metallic antimony along with a mixture of iron and sodium sulphide. The antimony was clean, and completely separated from the sulphides. The loss of antimony in the process amounted to 23·55 per cent.

Attempts were made to obtain antimony by smelting the refuse in a blast-furnace, although previous experiments had given no satisfactory results. The charge which was expected to prove most suitable consisted of 100 parts of refuse, 150 parts of puddling slag, and 40 parts of limestone. The smelting process was carefully carried out, but no metallic antimony was obtained. The product was a substance which looked like grey pig-iron (Roheisen), and was shown by analysis to consist of antimony, iron, and sulphur. With the same charge attempts were made to improve the result by better heating of the furnace, and increasing the force of the blast. By these means the product of the first tapping was found to contain 40 per cent. of antimony, and of the last tapping, after three days' work, 60 per cent. of antimony with a small quantity of metal separating from the mass. This was the best result obtained. W. T.

Damage done to Barley by Sprouting in the Field (*Dingl. polyt. J.*, **230**, 288).—According to the researches of Lawrestein and M. Marcker (*Zeit. Schrift für Spiritus Industrie*, 1878, s. 62) *sprouted barley* contains of matter soluble in water 18·64 per cent., the *normal barley* 11·62 per cent., the chief difference being in the large amount of dextrose and maltose contained in the former. For distillery purposes the sprouted barley is just as suitable as the other, but it is not suited for the manufacture of starch.

The nutritive value of the grain is essentially reduced by sprouting. W. T.

Aëration of Must. By A. Blankenhorn (*Chem. Centr.*, 1879, 31).—Aëration of must tends to decrease the amount of nitrogen in the finished wine, and so to prevent tendency to disease. Aëration is recommended in the case of all wines, even the poorer varieties. M. M. P. M.

Recovery of Sugar from Calcium Saccharates. By A. Dreverman (*Chem. Centr.*, 1879, 46).—Crystallisable sugar may be obtained from the compound of sugar and lime (or strontia or baryta) formed in Scheibler's refining process, by suspending it in water, adding magnesium sulphate in quantity rather less than is required for complete decomposition, and again adding a little of the calcium saccharate until an alkaline reaction is attained. The magnesium sulphate is added in concentrated solution. Magnesia and calcium sulphate are precipitated, and carry down with them the greater part of the colouring matter present. This method has the advantage over that of pre-

cipitation with carbonic acid in being much more rapid; the syrups are also more completely defecated, and it is more economical. If alcohol was present in the original substance, it should be removed by distillation *after* filtration from calcium sulphate, &c. According to the author, the sulphates of other bases, as alumina, iron, and zinc can be substituted for magnesium sulphate. M. M. P. M.

Nitrogenous Constituents of Cocoa. By G. W. Wigner (*Analyst*, 1879, 8—9).—Cocoa has been accounted a very nutritive food on account of its albuminoïd constituents having been calculated from the total nitrogen obtained on combustion with soda-lime. The author has estimated the nitrogen separately in the coagulable albuminoïds and in the non-coagulable matters. The former nitrogen alone probably represents flesh-forming matter, the latter being present in alkaloïds and in nitrates and nitrites. In the best samples of cocoa 78·5 per cent. of the total nitrogen was present in coagulable substances. The average of the samples of entire beans gave 57·6 per cent. of the nitrogen as present in coagulable bodies, whilst in one sample of prepared cocoa the proportion was as low as 39 per cent., and in one sample of entire beans only 50 per cent. Hence, until the nutritive value of non-coagulable nitrogenous bodies has been proved, cocoa must rank lower than it has hitherto done in the scale of foods. F. C.

Some Experiments with Silicated Carbon and Spongy Iron Filters. By G. W. Wigner (*Analyst*, 1878, 338—341).—Comparative experiments were made to ascertain the purifying effects of these filters on water contaminated partly by infiltration from the sea and probably also by surface drainage. That from the silicated carbon filter was preferred for drinking purposes, it was more free from flatness, and offensive taste and smell. It was harder than that which had passed through spongy iron, but possesses less permanent hardness. The most important results noted were that whereas the carbon filter removes albuminoïd ammonia, the iron filter produces a large quantity of ammonia, and a proportion of albuminoïd ammonia so large that it would undoubtedly lead to the water being condemned when analysed by Wanklyn's method. F. C.

Influence of the Chemical Composition of the Water used in the Preparation of Raw Silk. By L. Gabba and O. Textor (*Deut. Chem. Ges. Ber.*, **12**, 17—21).—In the manufacture of raw silk, the cocoons are immersed in water, with the object of softening but not of dissolving the natural gum by which the threads are held together. Raw silk owes its colour, strength, and beautiful appearance to the presence of its soluble constituents. When soft water is used in winding, the silk is inferior in strength, colour, and general appearance to that obtained when hard water is employed. This is explained by the fact that the soluble constituents of the silk are more rapidly dissolved by the soft than by the hard water.

Soft water can be improved for spinning purposes by the addition of gypsum, magnesium sulphate, and sodium carbonate: but since the silk spun with hard water always contains small particles of lime, it

is advisable not to use hard water in spinning silk which is to be dyed a light colour, as the piece is apt to be marked. W. C. W.

Methylaniline. (*Dingl. polyt. J.*, **5**, 230—245, 251, and 351—355).—Methylaniline as a name for the commercial product is correct in so far only as it implies a methylated aniline, as it is a mixture consisting chiefly of dimethylaniline, $C_6H_5(CH_3)_2N$, together with monomethylaniline, $C_6H_5.CH_3.HN$, aniline, toluidine, methylated toluidines, &c.

The quickest method of ascertaining the fitness for use of a methylaniline is by the distillation of a fixed quantity of the mixed bases under conditions which are always identical, just in the same way as the value of crude aniline is determined.

100 c.c. are sufficient, if during distillation the fluid passing over is observed at intervals of 1° in order to ascertain to what extent and in what direction essential uniformity or variation exists in the mixture of bases under examination. A methylaniline which contains a certain bulk of aniline will give a corresponding quantity boiling at a lower temperature; another mixed with a higher homologue will betray the fact by a corresponding rise in the boiling point at which a given quantity has come over; whilst in a third, a sudden change in the boiling point will show the presence of another base of relatively high boiling point.

The results of several such distillations are given in tabular form, and are of essential importance for testing the methylaniline used for the production of violet. In one series of experiments the methylaniline was produced by passing methyl chloride into boiling aniline, in others it was obtained from aniline hydrochloride and wood spirit under pressure. Whether the production of methylaniline could be carried out on a large scale by means of the methyl chloride reaction has not been ascertained, but it can scarcely be doubted that the results would be less satisfactory than those obtained by the treatment of aniline hydrochloride with wood spirit in closed vessels at a high temperature.

The technical value of a methylaniline is at present measured by the proportion of violet obtained, but every oxidation process does not produce the maximum of violet from all methylaniline, and consequently this test can be applied only when the violet is obtained by the most favourable process. The change into violet was effected in one instance by the treatment of the methylaniline with copper chloride and potassium chlorate; in another by the treatment of the hydrochloride with freshly prepared oxide of copper alone. One of the results obtained was that two methylanilines of very different composition yielded almost the same amount of colouring material.

The preparation of methylaniline on a large scale is effected in autoclaves made either of strong cast-iron enamelled inside, or of copper protected internally by gilding or enamel, and which must be capable of withstanding a pressure of 50 atmospheres: the copper vessels although dearer at the first fitting up are to be preferred. The lids are screwed on and made air tight. Each vessel is fitted with a manometer indicating 100 atmospheres, and a thermometer within a gilt copper tube

so arranged as to dip into the contained liquid. The vessel is supported in a wrought-iron air-bath, so as not to come into direct contact with the fire, and the bath is fitted with two thermometers which indicate the temperature low down and high up in the bath. The fire is so arranged as to be easily regulated. A strong heat is applied until the commencing pressure and the rise of the inner thermometer indicate the beginning of the reaction. The heating is then moderated until the maximum pressure of 20 to 25 atmospheres is reached: it is then moderated still more, and again increased after two or three hours. This increase in the heating does not again raise the pressure in the vessel, and the temperature as shown by the inner thermometer is not nearly so great as that in the air-bath. It is suggested that the difference in temperature may be reckoned as the equivalent of the chemical work done, inasmuch as any chemically indifferent mass heated for many hours in the same way would acquire the same temperature as that of the air-bath.

The aniline hydrochloride used in the process must be quite neutral, and as dry as possible. In this condition, it forms a crystalline somewhat hygroscopic mass.

The wood spirit used should have a sp. gr. of ·815 to ·820, equal to 95 per cent. of methyl alcohol, and be free from acids, ethereal salts, acetones, and the like.

The method of obtaining methylaniline carried out by the firm of Brigonnet and Co., at St. Denis, is described. The peculiarly constructed autoclave used in the process is charged with aniline and milk of lime, or lye, and methyl chloride passed in in quantity corresponding with the equation: $C_6H_5.H_2N + Ca(OH)_2 + 2MeCl = C_6H_5Me_2N + CaCl_2 + H_2O$. In this process the pressure is never greater than 6 atmospheres, nor the temperature above 100°. The author thinks that if methyl chloride could be obtained at a sufficiently low rate, this process would supersede every other in the manufacture of methylaniline. W. T.

Formation of Aniline-black by Chromate in Presence of Chlorates. By S. Grawitz (*Compt. rend.*, **88**, 389—391).—This is an answer to Witz (*ibid.*, 30 December, 1878), refuting his statement that the presence of chromates is injurious to the formation of aniline-black, and showing that it is necessary to have the solution slightly alkaline with ammonia, whereby the reduction of the chromates by the aniline salts and the action of the free acids on the fabric are prevented. Moreover the chromium mixture does not undergo any change in solution, but the black developes as it dries on the fabric. It can also be used along with other colours as a steam black.

L. T. O'S.

Patents.

No. 2948. *July 24th*, 1878. F. G. Vedova, of Smyrna. **"Improvements in the Manufacture of Materials containing Tannic Acid."**

The inventor takes the peculiar excrescences found on the oaks in Asia Minor and neighbouring countries, also the young shoots, acorns, and leaves of the same trees, and after washing the excrescences with a weak solution of sodium carbonate, in order to remove their gummy coating, pulverises and compresses the materials, and exports the products under the name of "vedovine." Another product is obtained by extracting the tannic and gallic acids by means of hot water, and evaporating the strained infusion to an extract. J. M. H. M.

No. 3341. *August 24th*, 1878. J. P. Rickman, of London. **"Manufacture of Ammonia."**

A project for the manufacture of ammonia from the nitrogen of the atmosphere. Inclined retorts, filled with oxidisable matter such as coke, are heated to about 1,000° F., and a mixture of steam and air in suitable proportions is driven through the red-hot mass. Any ammonia formed passes out of the top of the retort, and is collected in water or dilute acid. Another method is to saturate the coke with potassium carbonate and blow in air alone, the retort being heated to 1,800° F. After a certain time it is allowed to cool down to 1,000° F., when a mixture of steam and air is injected which decomposes the cyanogen at first formed, with production of ammonia.

J. M. H. M.

No. 5016. *December 7th*, 1878. H. J. Haddan. **"Treating Ores containing Silver and Copper."** (Communicated by J. de Baxeres de Torres and A. Drouin, both of Madrid.)

This patent is for the chloridising of silver ores in the wet way by means of an acidulated solution of common salt (or other chloride), instead of, as in the dry way, hitherto practised, by roasting with salt. Ores containing sulphur and arsenic are roasted previous to the treatment with salt solution; a little black oxide of manganese is added to facilitate both the roasting and the chloridising processes. Any copper contained in the ores is dissolved by the acidulated salt solution, together with the silver chloride formed, and from this solution the silver is precipitated by metallic copper, and the copper by metallic iron. J. M. H. M.

ERRATUM.

After last line, p. 421, insert.

On adding alcohol the lime salts produced by destruction of the glucose are precipitated.

4. To precipitate lime, salts, and other impurities from syrups which have been treated by the "alum process," previously patented by the inventors (1871, No. 2090).

Methyl alcohol or methylated alcohol may be used for these purposes instead of common alcohol.

General and Physical Chemistry.

Photographed Spectra of Oxygen and Hydrogen. By H. W. Vogel (*Deut. Chem. Ges. Ber.*, **12**, 332—334).—The author has succeeded in photographing the spectrum of pure oxygen enclosed at low pressures in Geissler tubes, through which the ordinary induction spark was passed. He employed for the purpose dry plates coated with silver bromide in gelatin, such plates being found to be much more sensitive than either wet plates or ordinary collodion dry plates. An exposure of two hours was found sufficient. The spectrum exhibited the following lines, or rather shaded bands, previously described by Paalzow (*Monatsber. Berlin, Akad.*, 1878, 205); $O\gamma$ between b and ϵ (Fraunhofer), $O\delta$ close to F, and $O\epsilon$ between F and G, the first very faint, but the last extremely distinct, rays of the refrangibility of $O\epsilon$ acting most powerfully upon silver bromide. Besides these, there was a band of extraordinary intensity, $O\eta$, near to Fraunhofer's line h, and a double band $O\varsigma$ near to G. All these bands were sharply defined at the side towards the red end, but shaded off towards the violet end of the spectrum. In addition to the foregoing, there appeared a series of faint shaded bands between $O\delta$ and $O\epsilon$, and a series of more distinct bands between $O\epsilon$ and $O\eta$, and beyond the latter in the direction of the ultra-violet, and two faint bands beyond H'' in the ultra-violet. Under a magnifying power of eight diameters, the whole of the bands were resolved into extremely fine lines, hundreds in number, closer together at the more sharply-defined side of the bands. The positions of the more important bands were determined by comparison with a solar spectrum photographed on the same plate. The following are the wave-lengths (taken from Angström's tables) of the bands measured when they were sharpest, *i.e.*, at the side of least refraction: $O\epsilon$ 4505, double band $O\varsigma$ 4390 and 4375, $O\eta$ 4125.

Photographs of the spectrum of hydrogen (obtained by electrolysis and by heating potassium formate) exhibit perfectly the three known hydrogen lines in the blue and violet, and also a red line $H\alpha$ coincident with the line C of the solar spectrum, and a number of other lines. The author states that the hydrogen line coincident with the line h of the solar spectrum is visible with the naked eye, even when the ordinary induction-current is employed. This is contrary to the experience of Lockyer, who asserts that this line is visible only at a very high temperature, such as is produced by the introduction of a Leyden jar into the circuit of the induced current, and who partly bases his hypothesis of the decomposition of hydrogen at high temperatures on this circumstance. J. R.

Blue Flame from Common Salt. By A. P. Smith (*Chem. News*, **39**, 141).—The blue flame produced when common salt is thrown on a hot fire is most probably due to hydrochloric acid; for

it is produced not only with sodium chloride, but also with $BaCl_2$, $SrCl_2$, KCl, NH_4Cl, Hg_2Cl_2 and HCl.

The author has roughly mapped the spectrum of the "chloride flame," and finds that it is characterised by a series of double bands in the green, blue, and violet, the least refrangible of each pair being most prominent. The four pairs in the violet are especially prominent; there are also two red bands and one orange. He has proved that chlorine is necessary to the production of the flame, and he has not been able to obtain it in the absence of hydrogen; moreover, the red H line is present, and the spectrum of pure chlorine is very different. The author hopes to be able to photograph the different spectra, and thus obtain more definite results.

L. T. O'S.

Effect of Heat on Mercury Di-iodide. By G. F. Rodwell and H. M. Elder (*Chem. News*, **39**, 56).—The methods of experiment are detailed. The red octohedral variety of mercuric iodide changes to the yellow prismatic form at 126°, with absorption of heat. Before the melting point of the iodide is attained, the yellow variety changes to deep red-brown; when fused, the liquid iodide has the exact colour of bromine. Distinct cracking sounds are heard during the continuance of the molecular changes.

The red iodide expands slowly up to 126°, when rapid expansion takes place without further rise of temperature. When the change is complete, regular expansion occurs under a higher coefficient than before the change, and is continued until the melting point is reached.

Coefficient of cubical expansion for 1° C. from 0° to 126° = 0·0000344706. During the change from the red to the yellow form, the iodide increases in bulk to the extent of—0·00720407.

Coefficient of cubical expansion for 1° C. from 126° to melting point = 0·0001002953. If a molten mass of mercuric iodide were to cool from 200° to 0°, the volume at varying temperatures would be as follows:—

Vol. of liquid mass at 200°	=	1·1191147
,, solid ,, ,, ...	=	1·0190453
Vol. at 126° (yellow prismatic form)..	=	1·0115378
,, (red octohedral form)....	=	1·0043337
,, 0°	=	1·0000000

The sp. gr. of the iodide under different conditions is as follows:—

Sp. gr. at 0°	=	6·297
,, ,, 126° (yellow)	=	6·225
,, ,, 200° (liquid)	=	5·286
,, ,, 126° (red)	=	6·276
,, ,, 200° (solid).....	=	6·179

M. M. P. M.

Determination of Specific Gravities. By E. F. Peckham (*Chem. News*, **39**, 97—98).—The following method for the determination of specific gravities of liquids was found to yield successful results when the quantity of liquid was only 3 c.c. A cube of aluminium, about 1 c.c. in bulk, suspended by a fine platinum wire,

of known weight, is weighed first in the air, then just immersed in water, and finally in the liquid the specific gravity of which is to be ascertained. The difference between the weight in air and the weight in water gives the weight of water displaced by the cube, and the weight of an equal bulk of oil is ascertained in a similar way. The quotient of the weight of oil by the weight of water gives the specific gravity. This method admits of perfect control over volume and temperature, and of rapid execution. For non-corrosive liquids, aluminium is preferable to platinum, on account of its low specific gravity. L. T. O'S.

Vapour-density Determinations at High Temperatures of Substances which attack Mercury. By L. Pfaundler (*Deut. Chem. Ges. Ber.*, **12**, 165—169).—A known weight of the substance is volatilised in a glass cylinder filled with dry air at 0°, the capacity of which is determined, and the change in pressure produced is observed by means of a mercury-manometer in connection with it. In order to prevent the vapour from coming in contact with the mercury, the experimental cylinder is connected with the shorter limb of the manometer by a long-coiled capillary tube, or by a series of cylinders joined by capillary tubes. The substance having been introduced, the whole apparatus dried and cooled to 0°, and the mercury-level in the two limbs of the manometer having been made to coincide with the upper end of the shorter limb, the apparatus is sealed. Before applying heat, some of the air in the experimental vessel is caused to pass into the shorter limb of the manometer, by allowing a certain quantity of mercury to flow out of the latter. The volume of this mercury and the change in pressure being noted, the capacity of the experimental vessel and capillary tube may be calculated. While the substance is being volatilised, this air is gradually forced back into the cylinder by pouring mercury into the longer limb of the manometer; diffusion through the capillary tube is thus entirely prevented. Ultimately the mercury is again brought to the upper end of the short limb of the manometer and the pressure noted, the temperature being at the same time observed by means of an air thermometer similar in construction to the experimental apparatus. The difference between this pressure and that in the air thermometer obviously gives the vapour-tension of the substance; its weight, volume, and temperature being also known, its vapour-density may be calculated. A diagram of the apparatus is given. Ch. B.

Limits to the Application of the Method of determining Vapour-densities in the Barometric Vacuum. By J. W. Brühl (*Deut. Chem. Ges. Ber.*, **12**, 197—204).—From the results of a large number of experiments made with a Hofmann's vapour-density apparatus, specially constructed to withstand high temperatures, and using amyl salicylate (b. p. 270°) and methyldiphenylamine (b. p. 290—295°) as the heating liquids, the author concludes that it is in most cases useless to make vapour-density determinations at a higher temperature than the boiling point of aniline, 185°; certainly not higher than 220°: for, firstly, at temperatures approaching 300°, the vapour-tension of

mercury increases about 10 m.m. for each degree, and hence a serious source of error, owing to the difficulty of reading high temperatures with accuracy; and, secondly, the pressure of mercury vapour at these high temperatures (= 242·2 m.m. at 300°) becomes so great as quite to destroy the vacuum.

A series of experiments showed that it was impossible at 290—295° completely to vaporise substances such as diphenylamine, anthracene, anthraquinone, and alizarin, which boil at the temperature of boiling mercury. See also a previous paper by the author, *Ber.*, **9**, 1368.

Ch. B.

Dissociation of Chloral Hydrate. By B. Engel and Moitessier (*Compt. rend.*, **88**, 285—287).—In a previous note (this Journal, Abst., 1878, 719) the authors showed that the vapour-tension of chloral hydrate at the boiling point is greater than the atmospheric pressure. They answer objections raised by Troost to their method of experimenting. Whilst Troost concludes from his own and Berthelot's experiments that chloral hydrate exists as a definite compound in the gaseous state, Wurtz has shown (*Compt. rend.*, May 13, 1878) that dissociation is complete at the temperature at which its vapour-density is taken. The authors have devised a very simple experiment to show this dissociation. When chloral hydrate is distilled with chloroform (in which anhydrous chloral is soluble, and water insoluble), the chloroform passes over turbid, and, on standing, a layer of water rises to the surface, which gradually reunites with the anhydrous chloral dissolved in the chloroform, and the solution, soon becoming denser than the chloroform, sinks to the bottom. If the retort is connected with a receiver furnished with a narrow neck terminated by a stopcock, the clear chloroform may be drawn off from the distillate at intervals and returned to the retort. In this way the water is prevented from reuniting with the anhydrous chloral, and an excess of chloroform vapour is maintained in the retort. From 20 grams of chloral hydrate, about 2 c.c. of water were thus obtained. The chloroform was previously dried by distillation from calcium chloride, and the chloral hydrate over phosphoric anhydride in a vacuum: an excess of anhydrous chloral added to the mixture in the retort, does not prevent the dissociation. The dissociation cannot be due to chemical action, for boiling chloroform dissolves chloral hydrate without decomposition, and it crystallises out again on cooling. Carbon bisulphide may be substituted for chloroform, when the dissociation takes place at about 47°, instead of about 61°. The authors are continuing the study of the phenomena, to ascertain the conditions under which the dissociation of chloral hydrate commences. J. M. H. M.

Absorption of Gases by Charcoal. Part II. On a new series of Equivalents or Molecular Numbers. By R. Angus Smith (*Chem. News*, **39**, 77).—Charcoal absorbs gases in definite volumes, the physical action resembling the chemical. If the volume of hydrogen absorbed be taken as unit, the following numbers express the volumes of other gases absorbed under similar conditions:—

$O = 8$; $N = 4{\cdot}66$; $CO = 6$; $CO_2 = 22$; $CH_4 = 10$; $NO = 12{\cdot}66$.

Calculating the weights of these gases absorbed, a remarkable relation is found to exist in certain cases between these and the quantivalence of the atoms; thus, for oxygen $\frac{16^2}{2} = 128$; for nitrogen $\frac{14^2}{3} = 65{\cdot}3$, these numbers representing the weights of these gases absorbed, the number squared representing the atomic weight and the divisor the quantivalence of the elementary gas. The weight of CO_2 absorbed is equal to sp. gr. squared = 484. There appears to be here a new series of molecular numbers made by squaring our present chemical atomic weights, and by certain other divisions peculiar to the gases themselves; we have certainly a building up by volumes with the production of an equivalent of physical combination analogous to the chemical equivalent. M. M. P. M.

Supersaturated Solutions. By J. G. Grenfell (*Chem. News*, **39**, 141—143).

Catalysis. By T. Bayley (*Phil. Mag.*, [5], **7**, 126—429).—The ordinarily accepted views regarding catalytic actions are exemplified by the reactions of hydrogen peroxide. A peroxide is defined as an oxide in which one or more of the oxygen atoms are so held that in the presence of such a substance as hydrogen peroxide a strain occurs in the reacting molecules. Cobalt peroxide is produced by the action of an alkaline solution of hydrogen peroxide on a cobalt salt, and the whole of the hydrogen peroxide is reduced to water and oxygen. Lead and manganese salts give the same reaction, but nickel peroxide is not formed under these conditions. Nickel peroxide has, however, the power of decomposing hydrogen peroxide, but the lower oxide of nickel so produced is not again converted into the peroxide. Hence the decomposition of hydrogen peroxide by cobalt salts is a case of chemical catalysis, *i.e.*, it involves a series of decompositions and reformations. M. M. P. M.

Inorganic Chemistry.

New Compounds of Hydrochloric Acid with Ammonia. By L. Troost (*Compt. rend.*, **88**, 578—581).—In the course of his researches on the vapour-densities of ammonia compounds, the author has discovered a large number of curious compounds formed by dry ammonia with mineral and organic acids. Two of these, namely, hydrochloric acid compounds containing excess of ammonia, are described in this paper. They are obtained by cooling pure sublimed ammonium chloride (made by the union of perfectly pure and dry NH_3 and HCl gases) to certain temperatures in contact with a large excess of ammonia gas.

Tetra-ammoniacal hydrochloride, $HCl.4NH_3$, melts at 7°. The crystals are anhydrous, and do not belong to the same crystalline system as sal-ammoniac, since they polarise light. The tension of the

ammonia dissociated from this compound at different temperatures is given below; it increases rapidly with the temperature, but is constant for the same temperature as long as any of the salt remains undecomposed, whatever may be the volume of gas in contact with it.

Temperature.	Tension of dissociation.	Temperature.	Tension of dissociation.
−36°	140 mm.	−10·8°	555 mm.
−28·6	165 „	− 6·0	730 „
−27·0	180 „	0	1035 „
−23·0	240 „	+ 3	1256 „
−20	310 „	5	1415 „
−17·7	360 „	6	1480 „
−16	395 „	7	1660 „
−13	485 „	8	1800 „

Hepta-ammoniacal hydrochloride, $HCl.7NH_3$ melts at − 18°, the liquid presenting all the characters of superfusion. About − 40° it solidifies to a translucid crystalline mass of a different aspect from the preceding salt, into which it resolves itself by dissociation. The dissociation tensions at different temperatures are as follows:—

Temperature.	Tension of dissociation.	Temperature.	Tension of dissociation.
−36°	580 mm.	−27°	895 mm.
−33	665 „	−25	980 „
−31·1	750 „	−23	1060 „
−28·6	835 „	−21	1130 „

The compounds of HCl with NH_3 at present known constitute the series $HCl.NH_3$; $HCl.NH_3 + 3NH_3$; $HCl.NH_3 + 2(3NH_3)$. The author considers that in all probability the limit of this series is not yet reached. J. M. H. M.

Existence of Nitrous Anhydride in the Gaseous State. By G. Lunge (*Deut. Chem. Ges. Ber.*, **12**, 357—359).—The author has endeavoured to settle by experiment the disputed question as to the existence or non-existence of nitrous anhydride in the gaseous form. His experiments consisted in allowing pure liquid nitrous anhydride to evaporate from a vessel provided with two exit-tubes. The gas escaping from one of those tubes was absorbed directly by sulphuric acid, whilst that escaping by the other tube was mixed with varying quantities of oxygen, at temperatures ranging from 3·5° to 150°, and afterwards likewise absorbed by sulphuric acid. Since in the latter case any nitrogen tetroxide produced by admixture with oxygen must on absorption take the form of equal numbers of molecules of nitrosulphonic and nitric acids, it was easy to calculate from analyses of the absorption-liquids how much of the nitrous anhydride employed had been dissociated and in consequence entirely oxidised to nitrogen tetroxide ($2N_2O_3 = 2NO + N_2O_4$; and $2NO + O_2 = N_2O_4$), and how much had remained unaltered after admixture with air. In the analyses, the total nitrogen was estimated by the mercury process, and

the quantity of oxygen required to oxidise the whole of the nitrogen acids to nitric acids was determined by titration with permanganate. The results are given in the following statement, where the figures in the first line express the proportion of oxygen actually present, the amount required to oxidise the whole of the N_2O_3 to N_2O_4 being 1.

Oxygen present	1·2	1·7	1·7	1·8	3·0	3·5	3·6	4·3	4·7	10·5
Unaltered N_2O_3	72	71	75	54	37	66	36	25	22	8 p. c.
Temperature ..	60·5	70	4	15	62	3·5	153	103	17·5	17°

From the results, the author concludes (1) that nitrous anhydride is partially dissociated by evaporation, but that complete dissociation is not brought about either by the presence of a large excess of oxygen or by high temperatures; (2), that the tendency to dissociation is greater in presence of larger proportions of air, but is not affected by temperature. J. R.

Compounds of Hydrogen Phosphide with Cuprous Chloride, and its Estimation in Gaseous Mixtures. By J. Riban (*Compt. rend.*, **88**, 581—584).—Phosphoretted hydrogen is rapidly and completely absorbed by a solution of cuprous chloride in hydrochloric acid, a white crystalline compound being at first formed which redissolves on passing the gas in excess.

To obtain the crystalline compound in quantity, phosphoretted hydrogen prepared by the action of phosphorus on milk of lime is freed from the liquid phosphide by washing with fuming hydrochloric acid, then passed into a vessel cooled by water or ice, and containing a solution of cuprous chloride in hydrochloric acid. The solution soon becomes charged with a mass of colourless needles, which are rapidly separated by the filter-pump, and dried by pressure. They give on analysis the formula of *cuprosodiphosphonium chloride*, $Cu_2Cl_2.2PH_3$ or $P_2(Cu_2''H_6)Cl_2$, analogous to the cuprosodiammonium chloride of Dehérain.

Cuprosodiphosphonium chloride loses phosphoretted hydrogen rapidly at the ordinary temperature, absorbs oxygen, and darkens. Heated, it evolves a mixture of phosphoretted hydrogen and hydrochloric acid gases, and leaves a residue of copper phosphide. Cold water decomposes it according to the equation—

$$3(Cu_2Cl_2 2PH_3) = 4PH_3 + Cu_6P_2 + 6HCl.$$

On passing an excess of phosphoretted hydrogen into the cuprous chloride solution, the crystals at first formed redissolve, but the more phosphorised compounds thus produced are extremely unstable. As a mean result, 1 c.c. of Cu_2Cl_2 solution containing 0·2622 gram dry Cu_2Cl_2, absorbed 132 c.c. of PH_3; these numbers are intermediate between those required by the formulæ $Cu_2Cl_2.4PH_3$ and $Cu_2Cl_2.5PH_3$. A current of inert gas expels the whole of the PH_3 from its saturated solution in Cu_2Cl_2; heat produces the same effect, the gas evolved being pure, uninflammable, and containing only a little hydrochloric acid which may be removed by washing. Air should first be chased from the apparatus by a current of inert gas. As a saturated solution of PH_3 in Cu_2Cl_2 may be preserved without alteration in a closed

bottle, and furnishes about 80 times its volume of phosphoretted hydrogen, it is a very convenient source of this gas.

Phosphoretted hydrogen may be estimated with accuracy in gaseous mixtures free from carbonic oxide by absorption with a hydrochloric acid solution of cuprous chloride. The treatment with Cu_2Cl_2 should be repeated, and followed by agitation with potash solution. Mixtures of hydrogen and phosphoretted hydrogen, analysed by this method, gave very exact results.

Solutions of cuprous chloride in potassium chloride, and of cuprous iodide in potassium iodide, absorb phosphoretted hydrogen, with formation of a black precipitate of Cu_6P_2. Cuprous cyanide dissolved in potassium cyanide gives no reaction with phosphoretted hydrogen.

Arsenic and antimony hydrides are absorbed by cuprous chloride solution, giving black precipitates. This reagent may, therefore, be used in preference to silver nitrate when operating on these two gases over mercury. J. M. H. M.

Manufacture of Potassium Iodide. By E. Schering (*Chem. News*, **39**, 118).—The author points out the defects of the three methods in actual use for the preparation of potassium iodide, namely:—

(1.) Decomposition of barium iodide (prepared from barium sulphide and iodine) with potassium sulphate.

(2.) Action of iodine on caustic potash and ignition of residue with carbon to destroy iodate.

(3.) Decomposition of ferroso-ferric iodide with potassium carbonate. He prefers the last method of manufacture, as attended with least difficulties and loss. L. T. O'S.

Lead in Potassium Iodide. By E. Schering (*Deut. Chem. Ges. Ber.*, **12**, 156—158).—Commercial iodine frequently contains lead, and hence in the manufacture of potassium iodide the crystals last obtained are often contaminated with lead iodide, which cannot be removed by crystallisation. Such crystals are of a yellow colour, and are usually unsymmetrical combinations of the cube and octahedron.

Lead can be completely separated from its solution in potassium iodide only by means of hydrogen sulphide, when the solution is very dilute. Ch. B.

Action of Light of Different Colours on Silver Bromide impregnated with Various Organic Colouring Matters. By C. Cros (*Compt. rend.*, **88**, 379—382).—The film of silver bromide was prepared from a solution of collodion containing 3 per cent. cadmium bromide, and a silver nitrate bath containing 20 per cent. silver nitrate and washed free from all soluble matter. This was impregnated with an aqueous or alcoholic solution of the colouring matter, and in the latter case was washed free from alcohol. The colouring matters used were: (1), an alcoholic solution of chlorophyll; (2), extract of black currant; (3), aqueous extract of mallows; (4 and 5), alcoholic extracts of carthamin and turmeric; and (6), solution of hæmoglobin, or an aqueous extract of the clot of cow's blood. The coloured lights were

obtained by passing the rays through different coloured solutions contained in transparent cells.

With an orange light obtained by passing the rays through a solution containing cobalt chloride and potassium chromate, images were obtained on plates saturated with chlorophyll, extracts of black currant, mallows, and turmeric. The models were bottles filled with yellow, red, and blue liquids. The positives under these circumstances had the appearance of pure water with the yellow and red, but with the blue the same as with a black liquid.

With a green light from a solution of nickel nitrate, images were produced on hæmoglobin, turmeric, and carthamine, where the red liquid appeared black, and the yellow and blue remained colourless.

With the light obtained from an ammoniacal solution of copper sulphate, turmuric gave very fine positive images, the yellow only appearing black, whilst the blue and red remained colourless. Silver iodide behaves in a similar manner to the bromide.

The author and Desains have noted the spectra given by the above solutions, and find those of the mallow and black currant to possess active rays in the red and violet, whereas those in the green are inactive, the opposite being the case with carthamin, which gives a spectrum in which the green rays are the most active. Chlorophyll gives a spectrum containing active rays throughout its entire visible length and extending beyond.

E. Becquerel, with reference to the paper, calls attention to the results on the same subject obtained by Vogel (*Bull. Soc. Photo.*, **20**, 42, *Bull. Soc. Chem. Ber.*, 7th year, 344), and to his own researches on chlorophyll (*Compt. rend.*, **79**, 185, and *Bull. Soc. Photo.*, **20**, 333), in which he shows that images may be obtained on silver bromide saturated with chlorophyll in the infra-red rays. He also stated that his results tend to show that the colouring matter adhering to the film imparted to it that special action which itself exerts on the light.

L. T. O'S.

Action of Chlorine on Barium Hydrate. By J. Konigel-Weisberg (*Deut. Chem. Ges. Ber.*, **12**, 346—350).—Dry barium hydrate, BaH_2O_2, does not absorb chlorine, but in presence of water it takes up a quantity of chlorine increasing with the proportion of water, until the whole, or nearly the whole, of the baryta is saturated; *i.e.*, until 1 mol. of barium oxide has taken up two atoms of chlorine. It seems probable that the reaction consists primarily in the formation of hypochlorite and chloride, the former of which breaks up at once into chlorate and chloride. The product contains only a small proportion of hypochlorite, nearly all the chlorine being in the form of chlorate and chloride. The reaction may therefore be expressed by the equation: $6BaO + 6Cl_2 = 5BaCl_2 + Ba(ClO_3)_2$.

J. R.

Analysis of Bleaching Powder. By G. Whewell (*Chem. News*, **39**, 80).—A sample of bleaching powder containing Ca 30·88, Cl 58·13, O, &c., 10·99 p.c., absorbed the following quantities of moisture in the times stated :—

24 hrs.	48 hrs.	72 hrs.	96 hrs.	103 hrs.
25	41	52·3	64·9	69 p.c.

M. M. P. M.

Ultramarine. (*Dingl. polyt. J.*, **231**, 500—503).—*Violet and red ultramarine.*—For the preparation of violet ultramarine, Zeltner introduces hydroxyl into ordinary ultramarine. By passing dry halogens, especially chlorine, over ultramarine-blue or -green, heated at 300°, halogen derivatives of ultramarine are obtained. By passing sulphuric anhydride at 150° over ultramarine, a reddish sulpho-derivative is obtained, which with alkalis gives alkaline sulphates and violet hydrated ultramarine oxide. By heating ultramarine-blue or -green at 160—180° and passing chlorine and steam into the mass, the same oxide is formed. In both cases 100 kilos. ultramarine require 34 kilos. chlorine gas. By treating ultramarine-blue or -green with salts, which when heated produce water and halogens, and heating the mixture, violet ultramarine oxide is formed, and in the presence of ammonium salts violet ultramarinamide. When ultramarine is heated with a solution of calcium or magnesium chlorides a violet is obtained.

Another method is to expose ultramarine-violet at 130—150° to the action of nitric acid vapours. Concentrated nitric acid gives light-red to pink colours; dilute acid, however, gives a more intense and darker red ultramarine.

By treating ultramarin-blue, -green, or -white at a high temperature with acids, or with salts evolving acids on heating, air being excluded, purple or violet colouring matters are produced, which are transformed into red by continued heating with or without access of air and by further treatment with acids (R. Hoffman).

Ultramarine-blue.—Plicque concludes from his investigations that ultramarine is free from nitrogen, and is produced from an oxygen salt of sulphur, probably that of sodium or aluminium; since in sodium-silico-aluminate only part of the oxygen is replaced by sulphur on ignition in carbon bisulphide vapour, whilst in an excess of sodium the whole is replaced. By the action of sulphurous acid on this product, it replaces part of the sulphur in the sulphurated sodium-silico-aluminate and converts the sodium sulphide into sulphate. This, however, does not take place unless the mixture has been exposed for some time to a temperature of 750°; at 1,000° a black product containing aluminium sulphide is obtained.

According to Guimet, the proportion of sodium to silicon is the same in all ultramarines, the quantity of sulphur may vary by double the amount, that of alumina by one sixth. Under the microscope ultramarines form crystalline masses resembling one another.

Philipp's investigations (*ibid.*, **224**, 625) show that ultramarine-green and -blue may be distinguished by the quantities of sodium sulphide present. Ballin and de Forcrand in describing the preparation of yellow silver-ultramarine (*ibid.*, **227**, 215) mention that this crystalline substance when pure contains 46·63 per cent. of silver. Sugiura shows that ultramarine may be decomposed by carbonic acid. Plicque gives the following formula for the pure blue:—

$$\left.\begin{matrix}3SiO_2Al_2O_3NaS_2\\3SiO_2Al_2O_3NaSO_2\end{matrix}\right\}$$

and for the blue-violet product which yields violet and red with chlorine, the formula $4SiO_2Al_2O_3\left\{\begin{matrix}NaS\\NaSO_2.\end{matrix}\right.$ D. B.

Complex Oxides of Cobalt and Nickel. By T. Bayley (*Chem. News*, **39**, 81).—Solutions of cobalt and nickel salts in presence of excess of soda are oxidised by sodium hypochlorite, with formation of the oxides Co_3O_5 and Ni_3O_5 respectively. On boiling the liquid containing the cobalt salt, it is decomposed, with evolution of oxygen, and formation of an oxide intermediate between Co_2O_3 and Co_3O_5, and agreeing well with the formula $Co_{12}O_{19}$. The nickel peroxide, Ni_3O_5, decomposes more easily than the corresponding cobalt salt; when the liquid in which it is precipitated is removed, the moist oxide begins to undergo decomposition; and if the moist oxide is dried in vacuo over sulphuric acid, the residue gives numbers agreeing with the formula $Ni_3O_{11}9H_2O$. When the liquid in which the nickel peroxide Ni_3O_5 has been formed is boiled, the salt is decomposed, without formation of stable lower oxides, although probably the production of the oxide Ni_2O_3 marks a stage in the reduction.

The cobalt oxides Co_3O_5 and $Co_{12}O_{19}$ appear to be stable at a low red heat. The following hydrates of the former have been prepared—

$Co_3O_5 4H_2O$ (dried over sulphuric acid).
$Co_3O_5 3H_2O$ (dried at 100°).
$Co_3O_5 2H_2O$ (dried at 138°).
and probably $Co_3O_5 H_2O$ (dried at 300°). M. M. P. M.

Some new Salts of Uranyl. By R. Sendtner (*Liebig's Annalen*, **195**, 325—333).—The author has studied the behaviour of uranium towards cyanogen, ferrocyanogen, bromine, iodine, and more particularly selenic and selenious acids.

Compounds of Selenic Acid and Uranyl.—Hydrated uranic oxide is dissolved in dilute selenic acid, and the solution is evaporated to a syrup and left to itself at a temperature of 0° to 4° for a few days. Bright yellow masses of a wavellite structure are formed which deliquesce in warm air. This salt seems to consist of $(UO_2)SeO_4.SeO_4H_2 + 18H_2O$.

In the preparation of this body, another salt of a greener colour is also formed, which has approximately the formula $2(UO_2.SeO_4).SeO_4H_2 + 12H_2O$, and is probably a mixture of uranous and uranic salts. A saturated solution of the hydrated oxide in selenic acid when strongly concentrated yields a salt of the composition $UO_2SeO_4 + xH_2O$.

Uranylpotassium Selenate, $SeO_4(UO_2).SeO_4K_2 + 2H_2O$, is best obtained by adding potassium uranate to warm selenic acid as long as it dissolves and concentrating the solution. It is easily soluble in hot water, and does not change in air. *Uranylammonium Selenate* may be prepared in a similar way.

Compounds with Selenious Acid.—The body $SeO_3(UO_2).SeO_3H_2$ may be obtained by the action of selenious acid on hydrated uranium oxide, but more easily by boiling concentrated solutions of the hydrated oxide and uranyl chloride.

Uranylpotassium Selenite, $SeO_3(UO_2).SeO_3K_2$, is formed when potassium uranate is dissolved in warm selenious acid, and the solution is concentrated. It is insoluble. A corresponding *ammonium salt* may be prepared in the same way. It is of a deeper yellow colour and also insoluble. It is important in the preparation of these

double salts to avoid too great concentration: standing over sulphuric acid in a desiccator is quite sufficient. All attempts to obtain an iodine compound corresponding with uranyl chloride were unsuccessful, neither could double salts be obtained. Hydriodic acid seems always to act as a reducing agent in these cases. Uranium bromide, analogous to uranium chloride, could not be obtained from bromine or hydrobromic acid and uranous oxide, in spite of numerous attempts. *Uranyl bromide* $(UO_2)Br_2 + 7H_2O$, is formed when hydrated uranic oxide is dissolved in concentrated hydrobromic acid and the solution is concentrated. It is easily soluble. Like uranyl chloride it unites readily with other bromine-compounds to form double salts. These salts are most easily prepared by dissolving, *e.g.*, ammonium uranate in hydrobromic acid.

The *potassium salt*, $(UO_2)Br_2.2KBr.2H_{20}$, crystallises in rhombic plates of a yellowish-brown colour. To obtain it in the crystalline state, excess of acid must be present. The *ammonium salt* is exactly similar.

G. T. A.

Purification of Mercury. By J. W. Brühl (*Deut. Chem. Ges. Ber.*, **12**, 204—206).—The following method is recommended as being effectual and rapid. The impure metal is shaken twice or three times with an equal volume of a solution containing in one liter of water, 5 grams potassium dichromate, and a few c.c. of sulphuric acid. The shaking is continued each time until the red mercuric chromate first formed has disappeared, and the solution has become pure green in colour. After each operation the metal is washed in a stream of water sufficiently powerful to carry off a fine green powder which forms on its surface. It is finally washed with distilled water. A large quantity of mercury which had become almost solid from impurities was thus easily purified in the course of an afternoon. The loss of metal is trifling. Even pure mercury, shaken three times with the above mixture, lost only ½ per cent. in weight.

Ch. B.

Metallic Phosphides. By O. Emmerling (*Deut. Chem. Ges. Ber.*, **12**, 152—155).—Many metallic phosphides are decomposed by heat, and cannot, therefore, be obtained pure by the action of phosphorus on the metals at high temperatures under ordinary circumstances. Complete union, may, however, frequently be effected under pressure, as in the following cases.

The metals, in the form of wire or foil, were heated with phosphorus in sealed glass tubes 20 centimeters long, enclosed in iron tubes filled with magnesia. A dull red-heat was maintained for 8—10 hours, and the tubes were finally opened in an atmosphere of carbonic anhydride.

Copper phosphide, CuP, a pulverulent silvery mass, sp. gr. 5·14, insoluble in hydrochloric acid, oxidised by nitric acid.

Magnesium phosphide, a bluish-green mass, very unstable. When exposed to air rapidly oxidising to magnesium phosphate. Not analysed.

Silver phosphide, AgP, a black, very brittle mass. When ignited, metallic silver is left.

Cadmium phosphide, Cd_2P, a greyish, sometimes silver-white mass. Dissolves in hydrochloric acid giving off phosphuretted hydrogen.

Zinc phosphide, Zn_3P_2, a crystalline mass. The only one out of the

many phosphides of this metal which have been already described which the author could obtain.

Tin phosphides, SnP and SnP_2 (according to the quantity of phosphorus used). The first is tin-white, the second black and brilliant, cleaving into thin plates. Sp. gr. of SnP_2 = 4·91 at 12°. Not attacked by hydrochloric acid.

Aluminium and mercury were not attacked; iron only superficially.

Ch. B.

Mineralogical Chemistry.

The State in which the Precious Metals Exist in certain Minerals, Rocks, and Artificial Products. By E. Cumenge and E. Fuchs (*Compt. rend.*, **88**, 587—580).—*Pyrites.*—The authors have examined samples of auriferous pyrites from Berezowsk (Siberia), from Callao (Venezuela), and from Grass Valley (California). The Berezowsk pyrites yielded all its gold by amalgamation; the two others, both in the raw state and after roasting, yielded only insignificant quantities. Analysis gave the following results:—

	Gold. grm. per tonne.	Silver. grm. per tonne.	Antimony.	Arsenic.
Pyrites from Berezowsk..	100	—	absent	absent
Pyrites from Callao.....	300	—	0·001	,,
Pyrites from Grass Valley	150	250	0·0004	traces

From these figures the authors infer that the gold in the Callao and Grass Valley pyrites is combined with antimony, which prevents its amalgamation. The silver in the Grass Valley pyrites is probably combined with arsenic. A slightly auriferous mispickel from Guejar (Muleyhacen) also contained antimony. The authors do not conclude that antimony is the sole mineraliser of gold, the auro-argentiferous *tellurium* minerals of Hungary and Colorado being well known. They have, however, never found tellurium in pyrites, whilst on the other hand antimony exists in almost all the auriferous tellurium minerals.

Assaying.—The fusion with litharge never succeeds in collecting the whole of the gold into the button of lead obtained; but by fusing the ore with *grey antimonial copper*, every trace of gold may be obtained in a matt of antimonio-sulphide weighing at most one-tenth of the ore taken. This matt is best assayed by the *mixed method*, the exactitude of which the authors have demonstrated by rigorous synthesis. They propose this use of cupreous mineral in metallurgical operations for the extraction of gold.

Artificial products.—The subjoined table exhibits the results of experiments with various mixtures for obtaining glass coloured by gold:—

Name.	Composition of Glass.						Compound of gold introduced.	Nature of Glass obtained.			Remarks.
	Silica.	Potash.	Lime.	Magnesia.	Minium.	Gold.		Transparency.	Colour.	Behaviour in the Flame.	
Crystal No. 1..	40	9	—	6	45	0·25	Aurate of magnesia	Perfect.	Topaz yellow.	Coloured purple, transparent.	
Crystal No. 2..	43	10	—	4	43	0·30	Ditto	Perfect.	Yellow, deeper towards the bottom.	Coloured purple, transparent.	Some air bubbles, and a metallic button = $\frac{1}{4}$ the gold introduced.
Glass No. 4....	60	24	13	3	—	0·10	Ditto	Perfect.	Very pale green.	Completely decolorised.	Some air bubbles.
Glass No. 5....	57	30	13	—	—	0·25	Sodium aurosilicate.	Perfect.	Clear yellow.	Yellow, transparent.	10 p. c. of the potash was in the form of nitre.
Glass No. 6....	53	29	13	5	—	0·15	Aurate of magnesia.	Rather milky.	Honey yellow.	Coloured rose-white, opaque.	25 p. c. of the potash was in the form of nitre.
Glass No. 7....	57	28	13	—	Oxide of antimony 2	0·15	Double chloride of gold and antimony.	Perfect.	Yellowish white.	No change.	Excess of gold collected into a small button.
Glass No. 8....	55	26	16	6	—	0·50	Aurate of magnesia.	Troubled with metallic gold	Dichroïc, blue by transmitted light.	No change.	
Glass No. 9.... (argentiferous)	63	30	7	—	—	Silver 0·75	Silver nitrate.	Perfect.	White.	Clear yellow.	

Silicates.—A sample of chlorophyllite from the Alleghany mountains, with the formula $3SiO_2,Al_2O_3,3(CaMgFe)O$, was assayed by amalgamation for native gold. It contained 50 grams per tonne. Combined gold was then sought for by submitting both the mineral itself and the residue from the amalgamation process to the assay with grey antimonial copper free from precious metals. The mineral yielded the same amount of gold by this method as by amalgamation, and the amalgamation tailings gave only unweighable traces of gold arising from particles of amalgam which had escaped washing. There was, therefore, no combined gold in this chlorophyllite, which, however, contained 100 grams of silver per tonne in a combined state, which could not be extracted by simple amalgamation, but was obtained by amalgamation of the roasted matt resulting from fusion with grey antimonial copper. J. M. H. M.

Fluorite (Fluor-spar), from Evigtok in Greenland. By Klien (*Jahrb. f. Min.*, 1878, 407—408).—The fluorspar from the above locality occurs in greenish or nutmeg-brown coloured crystals, 1—3 cm. in size, and exhibiting the combination $\infty O\infty$. 0. These crystals are embedded in cryolite, whilst those at Kongsberg, Brevig, are embedded in calcite. Embedded fluorspar crystals are rarities. Those from Evigtok are often granular, and have an indistinct cleavage owing to their containing clefts which are often coated with deposits of galena or hematite. On being heated, they phosphoresce and become white or light red. The dark cryolite behaves in a similar manner, but the light coloured cryolite does not phosphoresce. Taylor, who first observed the occurrence of fluorspar in the cryolite of Greenland (*Quar. Jour.*, 1856, 140), concluded that the upper layers of the cryolite owed their loss of colour to the action of the trapp lying upon them, and Klien endorses this opinion. C. A. B.

A Decomposition of Hornstone. By A. Schmidt (*Jahrb. f. Min.*, 1878, 719—721).—The author described a peculiar change in the hornstone of the South-west Missouri (Die Blei und Zink-Erz-Lagerstätten von Südwest-Missouri), it having become a finely porous, hygroscopic, and earthy substance. It is quarried at the above-mentioned locality, and used for polishing. This hornstone, in its lower portions passes over into calcium silicate, and this latter substance leaves a very fine silica-skeleton on treatment with hydrochloric acid, whence the author considered it probable that the hornstone might originally have contained an intimate intermixture of calcite, which was afterwards dissolved out, thus leaving behind a porous mass of hornstone. This supposition was, however, erroneous, because the residual silica-skeleton of the calcium silicate never attained the fine porosity of the "polishing stone." No carbonic acid gas was evolved on treating the specimens with hydrochloric acid. *Microscopical examination.*—The hornstone consisted of a colourless or whitish transparent ground-mass, containing numerous, large, dirty-grey clouds, which were grouped together in certain spots, and often diminished the transparency of the ground-mass. Hydrated ferric oxide was the only enclosure, and it occurred in dark-brown specks.

From the above examination no conclusions can be drawn. *Chemical examination.*—A splinter of the hornstone in question was boiled for ten hours in a solution of caustic potash, and 45·9 per cent. of its weight was dissolved; whilst pure-powdered quartz, which was boiled in a similar manner, was not acted on at all. From this result, the author is of opinion that the hornstone consists of so intimate an intermixture of amorphous and crystalline silica, that the microscope cannot detect it; and, further, that the amorphous silica has been dissolved out by the action of an alkaline carbonate, more especially as he observed that in the quarry at Seneca the change commenced from above. C. A. B.

Quartz-Diorite from Yosemite. By A. Schmidt (*Jahrb. f. Min.*, 1878, 716—719).—The rock in question (which constitutes the great mountain range of the Yosemite Valley in the Californian Sierra Nevada) was described as granite by Whitney. Professor Cohen, of Heidelberg, considered it to be a quartz-diorite, resembling closely the "tonalite" from Monte Adamello, in the Southern Alps, described by vom Rath. *Microscopical examination.*—The Yosemite rock is a crystalline, granular mixture of predominating white felspar, grey quartz in grains and round masses, and dark-green to black hornblende. The latter mineral often accumulates in one spot, thus causing the otherwise light-coloured rock to exhibit irregular dark-coloured enclosures, sometimes several meters in diameter. Occasionally the felspar exhibits a twin-striation. Biotite is also present in certain spots in large laminæ and crystals, whilst in other places its presence cannot be detected microscopically. Yellow titanite crystals are often found in this rock, 4 mm. in length. *Microscopical examination.*—The felspar consists mostly of plagioclase, exhibiting a distinct twin-striation, and also two other kinds of striation, one of which is caused undoubtedly by cleavage cracks, whilst the cause of the other is doubtful. Some of the felspar crystals exhibit a fine zonal structure; others again are tolerably fresh and entirely free from striation, but it could not with certainty be ascertained whether the latter crystals were those of orthoclase or not. The enclosures observed in the felspars were (1) isolated, well-developed plagioclase crystals, some exhibiting hexagonal outlines, and others quadratic or rectangular outlines with banded striation (microline); (2) rare isolated light-green hornblende crystals and delicate biotite and specular-iron laminæ; (3) magnetite grains accumulated in certain spots and always accompanied by colourless, highly refractory crystals which are attached to the magnetite, these being sometimes "short-prismatic" and sometimes rounded off; (4) numerous colourless, thin, prismatic microlites, with obtuse domatic or pyramidal terminals, which are irregularly distributed, and do not exhibit a distinct basal cleavage; (5) rare brownish-yellow titanite crystals; (6) light-yellow rods and granular masses of epidote in decomposed felspar, sometimes with well-defined crystal outlines, and at other times surrounded with yellow specks.

The felspars are decomposed and cloudy in many places. The hornblende in thin sections is dark bluish-green to yellowish-green in colour, strongly pleochromatic, and often has grains of magnetite

attached to it. The biotite is mostly brown, and strongly pleochromatic, often exhibiting either clefts, or an undulating alternating green and brown band-like striation, with a strong light-absorption. Quartz is present in large amount, disseminated in cracked masses, which enclose isolated quartz-crystals, exhibiting hexagonal outlines. It also encloses a few irregularly distributed, mostly non-mobile fluid-pores of various sizes and shapes, but a few mobile globules were observed in some very small, round "pores." Cohen also detected trichites in some of the quartz grains. The specimens examined by the author were taken (1) from the neighbourhood of the Nevada Falls at the east end of the Yosemite Valley; (2) from the Yosemite Fall, two English miles to the west of the first locality. They were identical in composition, and, as the Yosemite Valley cuts transversely more than 1,000 meters deep into the Nevada mountain range, it may safely be concluded that the kernel of the Sierra Nevada at that spot consists of a micaceous quartz-diorite, which differs from the Alpine "tonalite" only in containing a greater amount of hornblende, and a smaller and less evenly distributed amount of mica, the macroscopical and microscopical characteristics of the Yosemite rock and "tonalite" being almost identical. C. A. B.

Artificial Diopside, formed in a Bessemer Converter. By N. S. Maskelyne (*Phil. Mag.* [5], **7**, 133—134).—Crystals of diopside were found in hollows in the silica bricks lining a Bessemer converter which had been subjected to an intense and prolonged heat in contact with a moderately aluminous and siliceous magnesian limestone. Analysis gave the following results:—

FeO.	Al_2O_3.	CaO.	MgO.	SiO_2.
1·63	2·47	19·5 to 21·0	14·45 to 16·49	63·0 to 58·75

The excess of silica over that required by the formula $(Ca\frac{1}{2}Mg\frac{1}{2})SiO_3$ is doubtless present as a mechanical mixture, and is probably derived from the silica brick.

Small crystals of the diopside were found to have the forms m,{110}; b,{010}; o,{$\bar{2}21$}; s,{$\bar{1}11$}. M. M. P. M.

Enstatite from South Africa. By N. S. Maskelyne (*Phil. Mag.* [5], **7**, 135—136).—The rock forms boss-like hills at Korn Kopje, and at a place 12 miles south of Holfontein in the Witfontein Mountains, Transvaal.

Analysis showed the rock to contain:—

SiO.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.
53	2·6	9·27	2	25·5	6·6

The occurrence of enstatite in a pure and massive state has not been noticed previously. Its occurrence in the neighbourhood of the South African Diamond Mines is especially interesting, as the author has before asserted the enstatitic origin of the serpentinized mass of which the mines are composed. M. M. P. M.

The Enstatite in the Olivine Nodules of the Gröditzberg. By P. Trippke (*Jahrb. f. Min.*, 1878, 673—681).—Thin sections of the specimen examined by the author showed that it consisted of two laminated minerals, having a cleavage parallel to the pinacoïds alone. From the optical properties of the two kinds of laminæ, it was evident that one was rhombic and the other monosymmetrical, the former mineral being enstatite and the latter diallagite. The two minerals were intergrown in a manner corresponding to the twin law of pyroxene, the contact planes being the macropinacoïd of one individual and the orthopinacoïd of the other. The intergrowth is alternating and extremely regular, even the laminæ appearing like those of a polysynthetical twin formation, when examined under the microscope in polarised light. The laminæ vary from 0·01 mm. to 0·07 in thickness. Thin sections of the enstatite made parallel to $\infty\breve{P}\infty$ exhibit a very fine striation parallel to the vertical axis, due to the interpolation of long yellowish needles, which are principally developed in the plane of the macropinacoïd, their breadth being 0·0005 mm. in $\infty\breve{P}\infty$, and from 0·0006 to 0·0007 in $\infty\bar{P}\infty$. No other enclosures were observed in the enstatite except a few "glass-enclosures," which occur in connection with similar enclosures in the neighbouring diallagite. The enstatite laminæ were penetrated by cracks occurring at right angles to the striation and at regular intervals, giving the whole a somewhat fibrous appearance. The author is of opinion that these cracks are not "cleavage cracks," as some of them are continued over into the diallagite laminæ in an irregular manner by a film composed of rows of "glass-enclosures." The diallagite is very full of glass-enclosures, and occasionally encloses globules of liquid carbonic anhydride. The most remarkable enclosures in the diallagite were undoubtedly some small yellowish or brownish tabular crystals, which exhibited extremely sharply-defined outlines in section, and generally two "form types." The crystals of the first type were *elongated* parallel to the vertical axis of the diallagite, and had a length of 0·027 mm. and a breadth of 0·003 to 0·009 mm., whilst those of the second type were *curtailed* parallel to the vertical axis of the diallagite, and had a length of 0·0015 to 0·012 mm. and a breadth of 0·015 to 0·018 mm. The author submitted these enclosures to a very exhaustive, optical, and crystallographical examination, and found that they were monosymmetrical, and occurred in the following seven combinations, viz.:—(1) $P.4P.\infty\breve{P}\infty$. (2) $2P.\infty\breve{P}\infty.\infty\breve{P}\infty$. (3) $-4P.\infty\breve{P}\infty.\infty\breve{P}\infty$. (4) $P.2P.\infty\breve{P}\infty.\infty\breve{P}\infty$. (5) $2P.-4P.\infty\breve{P}\infty.\infty\breve{P}\infty$. (6) $2P.-P.\infty\breve{P}\infty.\infty\breve{P}\infty$. (7) $P.2P.4P.\infty\breve{P}\infty.\infty\breve{P}\infty$. From the above, there can be no doubt that the tabular crystals are those of pyroxene. They were found to consist of an opal-like substance, which was undoubtedly an infiltration, and the author concluded that the laminæ were nothing more than negative forms of diallagite filled up with opal-substance. The conclusions arrived at by him are—(1.) enstatite and diallagite occur in regular lamellar intergrowth on the specimens above referred to, the lamellæ of diallagite being interposed parallel to the macrapinacoïd of the enstatite; (2) the acicular and tabular forms in both minerals must be considered to be negative forms of the enclosing minerals, filled up with opal. C. A. B.

The Twin-formation of Phillipsite, from Sirgwitz. By P. Trippke (*Jahrb. f. Min.*, 1878, 681—698).—Streng described (*Jahrb. f. Min.*, 1875, 585) phillipsite from Nidda and Sirgwitz very fully, and concluded from his investigations that it crystallised monosymmetrical, and was almost identical with harmotome. He pointed out that, like the latter mineral, phillipsite exhibited a feather-like striation upon $\infty\breve{P}\infty$ ($\infty\bar{P}\infty$ if rhombic), a horizontal striation upon 0P($\infty\breve{P}\infty$), and a horizontal striation parallel to the combination edge of 0P with $\infty\breve{P}\infty$ ($\infty\bar{P}\infty$. with $\breve{P}\infty$). As Descloiseaux had proved that harmotome crystallised in the monosymmetrical system, Streng concluded that phillipsite was also a monosymmetrical mineral, occurring twinned according to the same laws as those of harmotome. Trippke submitted phillipsite twin-crystals from Sirgwitz to a thorough optical examination, and the results obtained by him prove undoubtedly that Streng's conclusion was correct, viz., that phillipsite crystallises in the monosymmetrical system, the twins occurring as "penetration-twins" in the following manner, viz., two simple crystals twin according to the law, "the twin-plane a face of $\breve{P}\infty$" (0P), the individuals being turned round an angle of 180° and penetrating each other; then two of these penetration-twins form a *double-twin*, according to the law, "the twin-plane a face of $\breve{P}\infty$." In addition to his confirmation of the above, Trippke ascertained that three of the above-mentioned *double-twins* form another twin, according to the law, "the twin-plane a face of ∞P. (P), the whole twin being built up of twelve individuals, divided into twenty-four portions. This polysynthetical twin-growth has taken place in such a way that the resulting form resembles exactly a double-twin, according to the first two laws given above, there being outwardly *no evidence* of the very complicated twin-formation. The author gives at great length the experimental results of his optical researches into the twin-formation of phillipsite, and appends some drawings of the various twins observed by him.

C. A. B.

Crystals of Amazonstone (Microline) from Pikes Peak, Colorado. By G. v. Rath (*Jahrb. f. Min.*, 1878, 406).—These crystals sometimes attain a size varying from 15 to 20 c.m., and have a light-green colour, which is more intense towards the surface. They are found simple and also in twins, according to the Baveno law, the most interesting being those found embedded in and growing upon a radiating foliated albite mass, accompanied by quartz and fluorspar. They are also found in drusy cavities in "graphic granite." Amazonstone is seldom pure, being generally penetrated by fine lamellæ of orthoclase and albite.

C. A. B.

Ferruginous Particles deposited by a Sirocco at Certain Places in Italy. By M. Tacchini (*Compt. rend.*, **88**, 613—614).—During the hot south-east wind of February 24th, 1879, atmospheric dust was collected at Palermo, Termini, and Naples. The Naples dust resembled that of Termini, the Palermo dust being of a lighter yellow colour, owing to its mixture with local dust. The dust contained spheroïdal globules of metallic iron from ·004 mm. to ·041 mm. in

diameter. These dimensions agree with those given by Meunier and Tissandier for the magnetic spherules found in the older rocks; also with those of the magnetic spherules found at the bottom of the sea on the coast of Tunis and Algiers, which increases the probability that the dust of February 25th came from Africa. The author believes that the dust called *meteoric*, found in places the most distant from each other, and in very diverse situations, on snow, &c., has often an origin similar to that of the sirocco dust, *i.e.*, a terrestrial origin.

J. M. H. M.

Analysis of the Water of the Mineral Spring at Suhl. By E. Reichardt (*Arch. Pharm.* [3], **14**, 252—264).—The temperature of the water of this new mineral spring is 12·5°, and it contains 24 c.c. of carbonic anhydride per 1,000 grams at 760 mm. bar.; the sp. gr. is 1·0074 at 20°. It is characterised by containing a large amount of calcium chloride in solution, a quantity which exceeds that in the Elisenquelle at Kreuznach by 1·035 grams per 1,000 grams. The analysis of the water made by the author is compared with that by Sonnenschein, and is as follows:—

In 1,000 grams of water are contained—

	Reichardt.	Sonnenschein.
Sodium chloride	4·1307 grs.	4·52847 grs.
Potassium „	0·5916 „	—
Lithium „	0·0176 „	0·00014 „
Cæsium „	—	trace
Calcium „	2·7670 „	2·97401 „
Magnesium „	0·1598 „	0·03825 „
Strontium „	—	0·00021 „
Magnesium bromide	0·0059 „	0·01288 „
Sodium iodide	trace	trace
Barium carbonate	0·0021 „	—
Strontium „	0·0019 „	—
Calcium „	0·0352 „	0·18588 „
Ferrous „	0·0003 „	—
Manganous „	0·0007 „	—
Magnesium borate	— „	0·00012 „
„ phosphate	—	0·00031 „
Calcium sulphate	0·3497 „	0·28760 „
Potassium „	—	0·06911 „
Organic matter	0·0496 „	—
Silica	0·0124 „	0·01200 „
Carbonic anhydride (combined)	0·1930 „	—

The apparent discrepancies depend on the different methods of calculating the results.

E. W. P.

Organic Chemistry.

Action of Nitrosyl Chloride on Unsaturated Hydrocarbons. By P. Tönnies (*Deut. Chem. Ges. Ber.*, **12**, 169—170).—Nitrosyl chloride, like nitrous anhydride, combines directly with unsaturated carbon compounds. Thus with *amylene*, the compound $C_5H_{10}NOCl$ is produced, and with anethöil, the body $C_6H_4(OMe)C_3H_5NOCl$. By reduction, the first of these is converted into amylamine, and the second gives a base having the constitution $C_6H_4(OMe)C_3H_6.NH_2$. The subject is being pursued. Ch. B.

Two New Isomerides of Cyanuric Acid. By J. Herzig (*Deut. Chem. Ges. Ber.*, **12**, 170—177).—When hexbromacetone, C_3Br_6O, is triturated with one-fourth to one-third of its weight of urea, and the mixture heated, two acids, isomeric with cyanuric acid, are the principal products. By regulating the heat applied, either of these may be produced in excess.

α-Cyanuric Acid.—When the temperature is raised by means of an oil-bath to 150—160°, carbonic anhydride and much bromoform are given off. If the bath be further heated to 180°, a violent reaction sets in, accompanied by a further evolution of bromoform. The crystalline mass left on cooling must be extracted with boiling water, the solution shaken with ether to remove hexbromacetone, and the crude acid left on evaporation recrystallised several times from boiling water, and washed with boiling alcohol. The crystals of the acid deposited from water have the composition $C_3H_3N_3O_3.H_2O$; by crystallisation from boiling nitric acid it is obtained anhydrous. The acid is tasteless. It sublimes without melting, and when heated in a glass tube gives off vapours of cyanic acid. Several of its salts are described. Some of them strongly resemble the analogous salts of ordinary cyanuric acid. The barium salt, obtained by adding barium hydrate to a boiling solution of the acid, is the most characteristic. It has the composition $C_3HBaN_3O_3.4H_2O$, containing 40·77 per cent. Ba. The barium salt of ordinary cyanuric acid prepared in the same way contains only 29·72 per cent. of barium. Acetic chloride, barium hydrate, and bromine have no action on this acid, and ethyl iodide does not react with its silver salt. Phosphoric chloride converts it into ordinary tricyanic chloride. Decomposition of its barium salt by boiling dilute sulphuric acid, or treatment with red fuming nitric acid, converts it into ordinary cyanuric acid.

β-Cyanuric Acid.—This second modification is obtained by the same process as the first, the temperature of the oil-bath not being allowed to rise above 170°. β-cyanuric acid crystallises from hot water in fine silky needles, which sublime when heated, but do not yield cyanic acid. It is insoluble in ether, but much more soluble in water and alcohol than its isomerides. Its copper-ammonium and silver-ammonium salts are undistinguishable from those of α-cyanuric acid. From the latter, however, it is sharply distinguished by being completely decomposed by boiling soda into carbonic acid and ammonia,

and by yielding with barium hydrate two new bodies not yet examined. Phosphoric chloride acts on it, but produces no cyanuric chloride.

In the preparation of these acids, especially of the β-acid, biuret may be substituted for urea, as might be expected when we consider the high temperature at which the reactions occur. In this case, the reactions may be expressed by the equation—

$$C_2O_2N_3H_5 + C_3Br_6O = 2CHBr_3 + C_3H_3N_3O_3,$$

and the resulting acids may have the constitution—

$$NH<\begin{matrix}CO.NH\\CO.NH\end{matrix}>CO, \text{ or } NH_2.CO.N<\begin{matrix}CO\\CO\end{matrix}>NH, \text{ or}$$

$NH_2.CO.NH.CO.N:CO.$

Ch. B.

Modifications of the Physical Properties of Starch. By F. Musculus (*Compt. rend.*, **88**, 612).—The author's conclusions are summed up in this note as follows:—Amylaceous matter may exist in the colloïdal and in the crystalloïdal states. In the former it is soluble in water; saccharifiable by ferments like diastase and by dilute boiling mineral acids; but easily undergoes changes which render it insoluble even in boiling water, and incapable of being attacked by ferments and by acids. It is coloured blue by iodine; the insoluble modification is coloured red or yellow by iodine. When it has been previously treated by ferments or dilute acids, it gives anew the blue reaction and becomes saccharifiable if acted on by concentrated sulphuric acid or caustic alkalis.

In the crystalloïdal state it may be obtained as isolated crystals easily soluble in cold water. These crystals agglomerate rapidly, and then become less and less soluble. Crystallisable starch thus undergoes the same modifications as colloïdal starch, but it remains soluble in water heated to 50° or 60°, and is always saccharifiable by ferments and acids. In isolated crystals it is not coloured by iodine; in dilute solution, iodine gives it a red colour; in concentrated solutions, violet or blue according to the concentration. It diffuses through parchment paper, although with difficulty.

The author compares the soluble and insoluble forms of starch with cellulose as it appears in young tissues and in cherry and plum stones respectively. J. M. H. M.

Crystalline form of the Stannmethyl Compounds and their Homologues. By M. Hiortdahl (*Compt. rend.*, **88**, 584—586). In their chemical behaviour, the compounds of stanndimethyl and its homologues resemble those of a diatomic metal, such as lead, whilst the compounds of stanntrimethyl and its homologues resemble those of the alkali-metals. The author's measurements are for the purpose of ascertaining whether this similarity extends to crystalline form and dimensions.

Stanndimethyl chloride and *stanndiethyl chloride* form rhombic

crystals, like those of lead chloride. Measurements of the proportions between the axes gave for

Stanndimethyl chloride	·8341 : 1 : ·9407
Stanndiethyl chloride.....	·8386 : 1 : ·9432
Lead chloride	·8408 : 1 : ·9990

The chloroplatinates corresponding with these two chlorides are not isomorphous; *chloroplatinate of stanndimethyl* forming splendid red rhombic crystals, with axes $a : b : c = ·8883 : 1 : ·9768$, whilst *chloroplatinate of stanntriethyl* forms tetragonal pyramids, in which $a : c = 1 : 1·1757$. By heating metallic tin with propyl iodide (b. p. 101°) at 150° in sealed tubes, and decomposing the iodide thus obtained by ammonia, the author has prepared *stanndipropyl oxide*, resembling in its reactions the corresponding oxides containing methyl and ethyl. The *stanndipropyl chloride* obtained from this forms magnificent colourless, rhombic crystals, differing from the previous chlorides as mercuric chloride differs from lead chloride. Stanndipropyl chloride forms very acute pyramids, with very perfect cleavage parallel to the base, resembling the very cleavable pyramids of mercuric bromide recently described by the author in the *Bull. de l'Acad. de Christiania*. Thus, for

Mercuric chloride	$a : b : c$	$= ·7254 : 1 : 1·0648$
Mercuric bromide	„	$= ·6817 : 1 : 1·0183$
Stanndipropyl chloride	„	$= ·6943 : 1 : \frac{1}{3}(1·0047)$

Stanndimethyl formate gives rhombic crystals, like the formates of lead, barium, and calcium:—

Stanndimethyl formate ..	$a : b : c$	$= ·7287 : 1 : ·4784$
Calcium formate	„	$= ·7599 : 1 : ·4671$
Barium formate	„	$= ·7650 : 1 : 2(·4319)$
Lead formate	„	$= ·7417 : 1 : 2(·4219)$

Stanndimethyl sulphate, analysed by Cahours, belongs to the monoclinic system. Its crystals consist of a rhomboidal prism, inclined at 74° 50′ with the base and the positive hemiorthodome, the vertical axis making an angle of 83° 75′ with the inclined axis, which is the longest. It is not, therefore, isomorphous with lead and barium sulphates, yet the lengths of its axes are sensibly the same:—

Stanndimethyl sulphate....	1·3213 : 1 : 1·6630
Barium sulphate	1·3127 : 1 : $\frac{1}{2}$(1·6352)
Lead sulphate	1·2915 : 1 : $\frac{1}{2}$(1·5728)

Chloroplatinate of stanntriethyl has been already described as crystallising in octahedrons (regular?), like chloroplatinate of potassium.

Stanntrimethyl sulphate forms extremely brilliant rhombic pyramids, for which $a : b : c = ·8872 : 1 : 1·0858$, a form having no analogy with that of the alkaline sulphates. *Stanntriethyl sulphate*, however, forms hexagonal prisms terminated by pyramids, whose dimensions are very like those of potassium and thallium sulphates:—

Stanntriethyl sulphate..	$a : a\sqrt{3} : c$	$= ·5773 : 1 : ·7217$
Potassium sulphate	$a : b : c$	$= ·5727 : 1 : ·7464$

J. M. H. M.

Action of Potassium Carbonate on Isobutaldehyde. By F. Urech (*Deut. Chem. Ges. Ber.*, **12**, 191—193).—When isobutaldehyde, prepared by oxidation of isobutyl alcohol, and hence containing acetone, is allowed to stand over potassium carbonate, it is converted into a thick, insoluble liquid, which may be freed from acetone by washing with water, and from unaltered aldehyde by the air-pump. This liquid may be distilled without change in a current of steam; by distillation alone, it is resolved into isobutaldehyde (thus easily obtained quite pure) and condensation products.

When the action takes place at 100°, isobutaldehyde, like valeraldehyde (*Ber.*, **8**, 369), yields agreeably smelling condensation-products of high boiling point, of which only one has yet been isolated. This body, $C_{12}H_{22}O_2$ ($= 3C_4H_8O - H_2O$) boils at 154°, and is nearly insoluble in water. On oxidation, it gives isobutyric acid and other products. Ch. B.

Preparation of Divaleryl. By J. W. Brühl (*Deut. Chem. Ges. Ber.*, **12**, 315—320).—The author has obtained this substance by the action of sodium on valeric chloride diluted with five times its bulk of ether. The crude product of the reaction was purified by distillation under reduced pressure. The pure substance forms a yellowish oil, of agreeable fruity odour, faintly recalling that of amyl alcohol. At ordinary pressures, it boils at 270—280°, with partial decomposition, but under the pressure of 80—100 mm. it distils unaltered at 210—220°. Being an easily alterable body, it is prepared only with difficulty.

Divaleryl is the fourth substance of its class as yet known with certainty, the others being dibutyryl, dicuminyl, and dibenzoyl. J. R.

Preparation of Methyl Formate and of Pure Methyl Alcohol. By C. Bardy and L. Bordet (*Compt. rend.*, **88**, 183—185).—A mixture of methyl alcohol and hydrochloric acid is poured into a flask containing sodium formate, previously dried at 140°, and powdered. A spiral tube surrounded with cold water connects the flask with a receiver, from which proceeds a second spiral tube, kept constantly cold. The flask is heated in a water-bath, cold at first, but gradually raised to ebullition, which temperature is maintained until the water surrounding the first spiral attains 45°; in a receiver connected with the second spiral, a liquid then collects, which, after the trace of hydrochloric acid possibly contained in it has been neutralised with soda, and it has been twice distilled over the water-bath, yields pure methyl formate (b. p. 32°). The methyl alcohol employed in this operation should be very pure, and especially should not contain impurities of lower boiling point. The methyl formate when saponified by soda, with proper precautions, yields aqueous methyl alcohol; perfectly pure, anhydrous, methyl alcohol may be obtained from this by rectifying it twice over potassium carbonate, twice over sodium, and finally over anhydrous phosphoric oxide. The sodium formate produced in the saponification may be used for the preparation of a fresh quantity of methyl alcohol. The operation succeeds equally well when lime is used instead of soda. R. R.

Physical Properties of some Methyl-compounds of 3- and 4-Carbon Acids. By G. W. A. Kahlbaum (*Deut. Chem. Ges. Ber.*, **12**, 343).—The author has prepared the following methyl-compounds, and determined their boiling points, specific gravities in relation to water at 4°, and refraction indices. All except the α-chloropropionate were obtained by passing hydrogen chloride into methylic solutions of the pure acids. The results were as follows:—

	Boiling point.	Sp. gr.
Methyl propionate	79·5	0·9578
„ α-chloropropionate .	132·5	1·0750
„ butyrate	101·0	0·9475
„ crotonate	120·7	0·9806
„ monochlorocrotonate	160·8	1·0933

The refraction indices were determined for the lines Hα, Na, Hβ (Fraunhofer's C, D, F), and Hγ:—

	Hα.	Na.	Hβ.	Hγ.
Propionate	= 1·3792	1·3812	1·3858	1·3897
α-Chloropropionate..	= 1·4206	1·4230	1·4282	1·4328
Butyrate	= 1·5227	1·5253	1·5318	1·5808
Crotonate.....	= 1·4107	1·4138	1·4221	1·4293
Chlorocrotonate	= 1·4560	1·4589	1·4676	1·4749

Other methyl-compounds are being examined. J. R.

Dibromocapric Acid. By C. Hell and P. Schoop (*Deut. Chem. Ges. Ber.*, **12**, 193—197).—Gäss (*Ber.*, **10**, 455, note) by oxidising a condensation-product of valeraldehyde, obtained an acid, $C_{10}H_{18}O_2$, named by the authors *amydecylenic acid*. This acid combines directly with bromine, forming a *dibromocapric acid*, $C_{10}H_{18}Br_2O_2$, which crystallises in monoclinic prisms (m. p. 135°), and cannot be sublimed unchanged when the quantity is large. Boiling with water or baryta-water decomposes it, a neutral oil of agreeable odour distilling over. It contains 34·6 per cent. of bromine. Caustic alkalis produce the same oil in smaller quantity.

Little is known about the action of alkalis on dibrominated acids. *Dibromovaleric acid* (from angelic acid) is decomposed by them into monobromobutylene, hydrobromic acid, and carbonic acid (Jaffe, *Annalen*, **135**, 302); but in the above reaction, carbonic acid could not be detected, and *monobromononylene* would contain 39 per cent. of bromine. Probably hydroxylated acids are formed. (See also Körner, *Annalen*, **137**, 234; Wichelhaus, *Jahresbericht*, 1867, 483; Tollens and Wagner, *Ber.*, **6**, 542). Ch. B.

Monochlorolactic Acid and Dichloropropionic Acid from Glyceric Acid. By Werigo and Melikoff (*Deut. Chem. Ges. Ber.*, **12**, 178).—By acting with phosphoric chloride on glyceric acid, and treating the product with alcohol, the authors have prepared the ethyl salts of the above acids; but, owing to the accompanying secondary products, the process is tedious. These acids are more readily obtained by heating glyceric acid in sealed tubes with either

one-half or four to five times its volume of hydrochloric acid solution saturated at 0°.

Monochlorolactic acid is a syrupy liquid, easily soluble in water, alcohol, or ether. It is decomposed by distillation, and is so unstable that its salts are prepared with difficulty. Barium chlorolactate alone has been obtained nearly pure. Ethyl chlorolactate also is easily decomposed by alkalis and carbonates. Ammonia converts it into a basic body resembling serine. Silver oxide converts it into glyceric acid.

Dichloropropionic acid is crystalline, and is identical with the acid prepared by oxidising dichloropropyl alcohol (allyl alcohol dichloride). Its ethyl salt has also been formed by acting with alcohol on the chloranhydride of glyceric acid. This ethereal salt is easily decomposed by bases, giving derivatives of monochloracrylic acid.

Ch. B.

The Amount of Water Contained in Crystallised Calcium Glycollate. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **12**, 464—465).—Various amounts of water of crystallisation have been assigned to this body (see *Jahresbericht*, 1862, 284; 1873, 537; 1874, 570). The author prepared a perfectly pure salt by decomposition of the basic calcium salt of glyoxylic acid, and found that the anhydrous glycollate consisted of $(C_2H_3O_3)_2Ca$, whilst the air-dried crystals were $(C_2H_3O_3)Ca + 3H_2O$, but he concludes that the number of molecules of water in the crystals varies with the temperature and concentration of the solution.

G. T. A.

Boiling Points of the Ethereal Salts of Hydroxy- and Alkyloxy-Acids. By L. Schreiner (*Deut. Chem. Ges. Ber.*, **12**, 179—180).

		I. *Glycollates.*				II. *Lactates.*		
		OH.	CH_3.	C_2H_5.	C_3H_7.	OH.	CH_3.	C_2H_5.
Ethereal salts.	OH	—	178°	199°	—	—	—	—
	CH_3....	151·2°	132·5°	152°	178°	144·8°	—	—
	C_2H_5 ...	160°	138·6°	158·4°	184·5°	154·5°	135·5°	155°
	C_3H_7 ...	170°	147°	166°	192°	—	—	—

III. *Butyrates.*

Ethyl α-hydroxybutyrate = 167°
„ methoxybutyrate..... = 148°
„ ethoxybutyrate = 168·5°
„ hydroxoisobutyrate..... = 151°
„ ethoxyisobutyrate = 155°

From this table it is seen that an ethereal salt of a hydroxy-acid boils 20° higher than its methoxy-derivative, and that the ethyl salts of a hydroxy- and an ethoxy-acid have nearly the same boiling point. Further, the boiling point of an ethereal salt rises 20° for each addition of CH_2 to the alcoholic radicle, but only 10° for a similar addition to the saline radicle. In the latter case the boiling points of the ethereal salts of the fatty acids rise 20°.

Ch. B.

Derivatives of Normal Methoxybutyric Acid. By E. Duvillier (*Compt. rend.*, **88**, 598—600).—From this acid and its salts, prepared as described in a previous paper (*Compt. rend.*, **86**, 1026, and this Journal, 1878, Abst., 662), the author has prepared the following derivatives:—

Ethyl methoxybutyrate, $CH_3.CH_2.CH(MeO).COOEt$, is obtained by heating a mixture of sodium methoxybutyrate (1 mol.) in alcoholic solution with ethyl iodide (1 mol.) at 100° in a closed vessel for some hours. The alcohol is removed by distillation, and the residue treated with water; the ethyl methoxybutyrate which separates is dried and rectified. It is a colourless mobile liquid, of burning taste and fragrant odour, insoluble in water, soluble in all proportions in alcohol and ether. It is lighter than water, and boils at 159—161°.

Methyl methoxybutyrate, $CH_3.CH_2.CH(MeO).COOMe$, is obtained by treating 1 mol. of methyl bromobutyrate with 1 mol. of sodium methylate dissolved in methyl alcohol. It is isolated and purified as described for the preceding compound, and is similar in appearance and properties. It distils between 145° and 155°. The methyl bromobutyrate required for its preparation is obtained by boiling together 4 parts of wood spirit and 5 parts of normal bromobutyric acid for six hours, adding water, washing the separated liquid with weak potash, and distilling from dry potassium carbonate. By repeating the treatment with potash, and distillation, the liquid distils over between 165° and 172°. It is denser than water and insoluble in it, but soluble in ether, alcohol, and wood spirit in all proportions.

Methoxybutyramide, $CH_3.CH_2.CH(MeO).CONH_2$.—Methyl methoxybutyrate is mixed with three times its volume of absolute alcohol saturated with ammonia gas, and heated at 100° in a closed vessel for several days. The resulting liquid evaporated in a vacuum over sulphuric acid deposits crystals of the new compound, which may be purified by several crystallisations from water, powdered, and dried between bibulous paper.

Methoxybutyramide forms slender interlaced needles, very soluble in water, alcohol, and ether. It melts at 77—78°, and must be dried in a vacuum, as it begins to volatilise below 100°. Heated more strongly, it boils and sublimes with slight decomposition. J. M. H. M.

Oxidation of Levulinic Acid. By B. Tollens (*Deut. Chem. Ges. Ber.*, **12**, 334—338).—The properties of levulinic acid as described by Grote and the author, agree exactly with those lately ascribed by Conrad (*Ber.*, **11**, 2177) to synthetic acetopropionic acid; and it having been shown by Nöldecke (*Annalen*, **149**, 232) that the latter body yields by oxidation succinic acid, the author has now submitted levulinic acid to oxidation for comparison. His results accord perfectly with those of Nöldecke, thus showing that levulinic acid is identical with acetopropionic acid, and that it contains five normally combined carbon atoms, as must also the carbohydrate from which it is produced. J. R.

Reaction of Dibromosuccinic Acid with Water. By E. Bandrowski (*Deut. Chem. Ges. Ber.*, **12**, 344—346).—The author finds

that dibromosuccinic acid is completely decomposed by boiling with water in the manner indicated by the equation $C_4H_4Br_2O_4 - HBr = C_4H_3BrO_4$. This equation, however, does not fully express the reaction, inasmuch as the formula $C_4H_3BrO_4$ represents two acids, one melting at 129—130° and the other at 172°. The former of these acids is produced by prolonged boiling of dibromosuccinic acid with $1\frac{1}{2}$ times its weight of water at ordinary pressures. The latter is produced on heating the dibromo-acid at 140° with water in sealed tubes. The acid melting at 129° was found to be identical with bromomaleic acid. The reaction is being more fully investigated. J. R.

Pyroracemic Acid. By C. Böttinger (*Liebig's Annalen*, **196**, 92—108).—When glyceric acid is subjected to dry distillation, the first portion of the distillate consists of a mixture of formic, acetic, pyroracemic, and pyrotartaric acid, and water. Glycuvic acid next passes over as a pale yellow-coloured oil, which solidifies on cooling to a crystalline mass; finally a thick dark oil distils over, containing pyrotartaric acid, and a syrupy acid which forms a barium salt of the composition $(C_3H_4O_3)_2Ba$.

Glycuvic acid melts at 83° and boils at 247°. It is deposited from a solution in warm water in crystalline scales, and from warm dilute alcohol in needles. The potassium salt, $C_8H_9KO_6$, crystallises in transparent prisms, which are hygroscopic; the barium salt, $(C_8H_9O_6)_2Ba + 2H_2O$, forms transparent six-sided crystals which are sparingly soluble in cold water; the calcium salt resembles calc spar in appearance.

Nitric acid converts glycuvic acid into oxalic acid, whilst on fusion with potash or on oxidation by chromic acid it yields acetic acid.

The author concludes (1) that the amount of pyroracemic acid formed in the dry distillation of glyceric acid is too insignificant to afford any clue to the constitution of pyroracemic acid; and (2) since pyroracemic and α-chloropropionic acids both yield the same sulpholactic acid (*Ber.*, **11**, 1561, and this vol., 45), pyroracemic acid is a ketonic acid of the rational formula $CH_3.CO.COOH$. W. C. W.

Dry Distillation of Ammonium Salts of Saccharic Acid. By Chichester A. Bell and E. Lapper (*Deut. Chem. Ges. Ber.*, **10**, 1961—1964).—When saccharate of ammonia is slowly decomposed by the heat of a paraffin-bath, it breaks up almost quantitatively into pyrrol, carbonic anhydride, ammonia, and water, $C_6H_{10}O_8.2NH_3 = C_4H_5N + 2CO_2 + NH_3 + 4H_2O$; and ethylamine saccharate is similarly decomposed, yielding ethyl-pyrrol in theoretical amount. No trace of any carboxylated derivative of pyrrol could be detected in either case. By these reactions, saccharic acid is distinguished from its isomeride mucic acid (see next Abstract). The difference may perhaps be explained by the different distribution of the hydroxyl groups in the molecules of the two acids, $C_4H_2(OH)_4(COOH)_2$. In saccharic acid, these may be nearer to the carboxyl groups than in mucic acid: hence the instability of the carboxyl groups, which are decomposed at a lower temperature than that at which they would become amidated.

Ch. B.

Pyrrol Derivatives. By Chichester A. Bell (*Deut. Chem. Ges. Ber.*, **10**, 1861—1868; **11**, 1810—1814).—When the mucates of the primary fatty amines are heated by means of a paraffin-bath, there are produced (1) alkyl-derivatives of pyrrol, and (2) the alkyl-amides of mono- and di-carboxylated derivatives of these pyrrols. Thus ethylamine mucate is decomposed as follows:—

(1.) $C_6H_{10}O_8.2NH_2.C_2H_5 = C_4H_4(C_2H_5)N + 2CO_2 + 4H_2O + NH_2.C_2H_5$,
(2.) $C_6H_{10}O_8.2NH_2.C_2H_5 = C_4H_3(C_2H_5)N.CO.NH.C_2H_5 + CO_2 + 5H_2O$,

and by the secondary action of nascent ethylamine from reaction (1),

(3.) $C_6H_{10}O_8.2NH_2.C_2H_5 + NH_2.C_2H_5 = C_4H_2(C_2H_5)N(CO.NH.C_2H_5)_2 + 6H_2O$.

Methylamine mucate undergoes a similar change, but the amylamine salt, apparently, is decomposed as in (1) and (2). *Methyl-*, *ethyl-*, and *amyl-pyrrol* are colourless liquids boiling at 112—113°, 131°, and 180—184° respectively (pyrrol boils at 133°). The first two resemble pyrrol; the last has a powerful and characteristic odour. They dissolve in strong acids, and exhibit the pyrrol reactions with fir-wood, mercuric chloride, &c. When boiled with strong hydrochloric acid they do not, however, deposit any solid substance, as pyrrol does. Potassium does not act on them; whereas with pyrrol, hydrogen is evolved and potassium-pyrrol, C_4H_4KN, is formed. According to Lubavin (*Zeits. f. Chem.* [2] **5**, 399), ethyl iodide reacts with potassium pyrrol, forming an ethyl-pyrrol boiling at 155—175°, and having peculiar properties. This is not the case; the product of the reaction being the ethyl-pyrrol described above.

Dimethyl-, *diethyl-*, and *diamyl-carbopyrrolamide* are beautifully crystalline bodies, melting at 89—90°, 43—44°, and 77° respectively. Heated at 120° with strong alcoholic potash, the first two yield fatty amines and *methyl-* and *ethyl-carbopyrrolic acids*, $C_4H_3(CH_3)N.COOH$ and $C_4H_3(C_2H_5)N.COOH$, melting at 135° and 78° respectively.

The third amide, however, only gives potassic carbonate, amylamine, and amyl-pyrrol, the corresponding acid being probably very unstable. Methyl- and ethyl-carbopyrrolic acids are also unstable, a solution of the latter in water behaving like supersaturated carbonic acid water, and rapidly giving off carbonic anhydride in contact with rough surfaces. Dilute acids, boiling water, and sublimation also decompose them. Their salts are generally very soluble.

Triethyl-dicarbopyrrolamide (from reaction 3) is crystalline and very stable, and melts at 229—230°. Strong alcoholic potash at 130° decomposes it into ethylamine and *ethyl-dicarbopyrrolic acid*, $C_4H_2(C_2H_5)N(COOH)_2$. This acid sublimes without melting at 250°, partially decomposing into pyrrol and carbonic anhydride. It is quite insoluble in water. Weak acids do not act on it: strong acids slowly decompose it.

Boiling dilute hydrochloric acid slowly dissolves ethyl-pyrrol, forming an insoluble amorphous base, yielding soluble uncrystallisable salts, and possibly having the composition $C_{16}H_{24}N_2O_2(3C_6H_9N + 2H_2O = C_{16}H_{24}N_2O_2 + NH_2.C_2H_5)$.

Bromine-water produces with ethyl-pyrrol a *substitution*-product,

$C_4Br_4N.C_2H_5$, melting at 90°. With diethylcarbopyrrolamide it forms a substitution-product, $C_4Br_3N(C_2H_5)CO.NH.C_2H_5$, and a soluble crystallisable oxidation-product having acid characters and, probably, the constitution $C_4Br_2O(OH).CO.NH.C_2H_5$. The dimethylamide yields similar bodies. In no case was an addition-product obtained analogous to Schiff's dibromacetylpyrrol, $C_4H_4Br_2N(C_2H_3O)$ (*Ber.*, **10**, 1502).

The mucates of secondary and tertiary amines do not yield derivatives of pyrrol by distillation. They give off nearly the whole of their bases in the free state, leaving tarry residues. This fact and the indifference of the alkyl-pyrrol bases to potassium and acid chlorides, confirm Baeyer's view of the constitution of pyrrol $\begin{matrix}HC:CH\\HC:CH\end{matrix}>NH$. During the distillation of ammonium mucate pyrrol is probably formed by the action of ammonia on two of the hydroxyl-groups of the mucic acid, water and the imide residue (NH) being produced. One of the carboxyl-groups may remain attached to the pyrrol nucleus, and so give rise to carbopyrrolamide. When the mucates of the fatty amines are decomposed, one or both carboxyl-groups may remain unseparated, as shown above.

Pyrrol is obtained synthetically in some quantity when the vapour of diethylamine is passed through a tube heated to incipient redness.

Ch. B.

Structural Formulæ of Aromatic Compounds. By E. Wroblevsky (*Deut. Chem. Ges. Ber.*, **12**, 161—163).—The author proposes to indicate the constitution of benzene derivatives by the positions of the lateral groups in their formulæ.* He adopts Beilstein and Kurbatoff's (*Ber.*, **10**, 270) classification of these derivatives into those with symmetrical, unsymmetrical, and consecutive groups. The following are the formulæ of the di-, tri-, and tetra-chlorobenzenes :—

Empirical.	Symmetrical.	Unsymmetrical.	Consecutive.
$C_6H_4Cl_2$	$C_6H_2ClH_2Cl$	C_6H_3ClHCl	$C_6H_3Cl_2H$
$C_6H_3Cl_3$	$C_6HClHClHCl$	$C_6H_2ClHCl_2$	$C_6H_2Cl_3H$
$C_6H_2Cl_4$	$C_6HCl_2HCl_2$	$C_6HClHCl_3$	C_6HCl_4H.

The formulæ of consecutive derivatives are distinguished from empirical formulæ by the atom of hydrogen written separately. The symmetrical and unsymmetrical derivatives might also be written—

Symmetrical.	Unsymmetrical.
$C_6(H_2Cl)_2$	$C_6H_2(HCl)_2$
$C_6(HCl)_3$	$C_6H(HCl)_2Cl$
$C_6(HCl_2)_2$	$C_6(HCl)_2Cl_2$.

When the substituted groups are of different kinds, they and the intervening hydrogen-atoms must succeed each other in the formulæ in the order of their arrangement in the familiar benzene "ring." For instance, $C_6H_2ClBrHI$ indicates (Cl : Br : I = 1 : 2 : 4), and $C_6H_2IClHBr$ denotes (Cl : Br : I = 1 : 3 : 6)), &c.

The same system may be applied to derivatives of naphthalene, the

* This is no novelty. See Kekulé's *Lehrbuch* [1866], vol. ii, pp. 516, 544; and Körner (*Gazzetta chimica italiana*, 1874, pp. 305—446).—Ed.

constitution of the 4-carbon group, which together with a benzene ring makes up its nucleus, being shown within parentheses. The carbon atoms in the conjoined rings are numbered right and left, beginning with one to which no hydrogen is attached. For instance, $C_6HClH_2(C_4IH_3)$ represents chloriodonaphthalene (I : Cl = 1 : 2′) in the notation adopted in this Journal. Ch. B.

Hydrocarbons produced by the Action of Methyl Chloride on Benzene in presence of Aluminium Chloride. By E. Ador and A. Rilliet (*Deut. Chem. Ges. Ber.*, **12**, 329—332).—In a former paper (*Ber.*, **11**, 1627; this vol., 228) the authors showed that the dimethylbenzene produced by this action consisted entirely of metaxylene and paroxylene. An examination of the hydrocarbons of higher boiling point formed at the same time led to the following results:—

The portion boiling at 150—170° was found to consist of two trimethylbenzenes, viz., mesitylene and pseudocumene. This was proved by examination of their nitro- and sulpho-derivatives.

The portion boiling at 185—204° consisted of two tetramethylbenzenes, chiefly durene, with a small proportion of a liquid body boiling at 185—190°, and yielding a dibromo-derivative melting at 199° and a crystalline nitro-derivative melting at 165°. The latter body is thought by the authors to be identical with the β-durene of Jannasch (*Ber.*, **8**, 355).

Amongst the products of still higher boiling points was pentamethylbenzene, a liquid boiling at 230°, crystallising in ice, and forming a sulpho-compound with sulphuric acid. Also, hexmethylbenzene, a white crystalline body melting at 153° and boiling at 260°, insoluble in concentrated sulphuric acid. J. R.

Succinyl-compounds of the Toluidines. By G. v. Bechi (*Deut. Chem. Ges. Ber.*, **12**, 320 — 323).—*Tolylsuccinimides*, $C_2H_4 : (CO)_2 : N.C_7H_7$.—The author has lately shown (*Ber.*, **12**, 25) that *orthotolylsuccinimide* is produced by the action of succinic acid on orthotoluidine. This substance, when pure, crystallises in glistening white needles, melts at 75°, and distils without decomposition at 338—340°, under the pressure of 733 mm. It is soluble in water, alcohol, chloroform, carbon bisulphide, benzene, and ether, but crystallises best from water.—*Paratolylsuccinimide* is obtained in the same manner from paratoluidine, and purified by crystallisation from water. It crystallises in fine white needles, melts at 151°, and distils at 344—345° under 733 mm. pressure. It is less soluble than the ortho-compound, from which it may easily be separated by crystallisation from hot water.

Tolylsuccinamides, $NH_2.CO.C_2H_4.CO.NH.C_7H_7$.—The *ortho-compound* is formed by the action of alcoholic ammonia on orthotolylsuccinimide at 100° in sealed tubes. It crystallises in glittering white laminæ, melts at 160°, and at a higher temperature is resolved into ammonia and tolylsuccinimide. The *para-compound* is obtained in a precisely similar manner, and differs from the foregoing only in being less soluble, and melting at 148°.

Tolylsuccinamic Acids, $COOH.C_2H_4.CO.NH.C_7H_7$.—The *ortho-acid* is

obtained by boiling orthotolylsuccinimide with baryta-water, and adding dilute sulphuric acid to the solution. On standing, it is deposited from the filtered liquid in white needles, which melt at 97°, and are resolved, by further heating, into water and tolylsuccinimide. Its *barium salt*, $C_{22}H_{24}O_6N_3Ba + H_2O$, forms an indistinctly crystalline granular mass.—The *para-acid* resembles the preceding in mode of preparation and properties, but melts at 157°. Its barium salt crystallises in brilliant white needles, containing 1 mol. of water.

Ditolylsuccinimides, $C_2H_4(CO.NH.C_7H_7)_2$.—These bodies are obtained by heating a mixture of 1 mol. of succinic acid with 2 mols. of pure orthotoluidine or paratoluidine on a sand-bath for some time, exhausting the resulting mass with water (which dissolves the monimide formed at the same time), and crystallising the residue from hot alcohol. The *ortho-compound* forms delicate white needles, which dissolve very sparingly in water, melt at 100°, and on further heating break up into orthotoluidine and orthotolylsuccinimide. The *para-compound* likewise crystallises in white needles, which melt at 256°.

J. R.

Reactions of Phenylphosphine. By A. Michaelis and F. Ditiler (*Deut. Chem. Ges. Ber.*, **12**, 338—340).—Phenylphosphine reacts with carbonyl chloride, when the vapour of that substance is slowly passed into it, in the manner indicated by the equation: $2COCl_2 + H_2PC_6H_5 = Cl_2PC_6H_5 + 2CO + 2HCl$. The product is pure phosphenyl chloride.

Phenylphosphine and carbon bisulphide, when heated at 150° in sealed tubes, react in the following manner:—$2C_6H_5PH_2 + CS_2 = (C_6H_5PHCS)_2S + H_2S$. The product, *phenyldiphosphorosulphocarbonic acid*, dissolves easily in carbon bisulphide and sparingly in alcohol, but not in water. It is not decomposed by prolonged boiling with alcohol. When heated *per se*, it gives off hydrogen sulphide, a dark-coloured resinous mass being left. The acid dissolves readily in alkalis, and is precipitated unaltered by acids. It is soluble also in potassium sulphide. Chlorine acts on it as follows:—

$$(C_6H_5PHCS)_2S + 6Cl_2 = C_6H_5PCl_4 + C_6H_5PSCl_2 + 2CSCl_2 + 2HCl.$$

A mixture of phenylphosphine and chloroform reacts violently with potash in alcoholic solution, potassium chloride being deposited. On evaporation the liquid leaves a large quantity of potassium phosphenylite. The entire reaction has not been definitely made out.

The dissimilarity between the foregoing reactions of phenylphosphine and those of aniline is attributed by the authors to the great affinity of phosphorus for chlorine and oxygen. J. R.

Behaviour of Metanitranisöil towards Ammonia. By H. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 155—156).—Metanitranisöil, unlike its isomerides, is not converted into nitraniline by aqueous or alcoholic ammonia at 200°. This result agrees with Körner's law (*Jahresbericht*, 1875, 365), that in benzene derivatives a nitro-group only exerts a loosening influence on halogen or other groups, when it is in the ortho- or para-position with respect to them. Ch. B.

New Mode of Formation of Ketones. By G. v. Bechi (*Deut. Chem. Ges. Ber.*, **12**, 463—464).—When sodium is added to a dilute ethereal solution of ethyl iodide and benzoic chloride (all in molecular proportions) a yellow precipitate is gradually produced. After about 48 hours the whole is treated with ether, and the ethereal solution evaporated. The brown liquid thus obtained is treated with dilute potash solution, and submitted to fractional distillation. Between 205—210° a bright yellow oil passes over which refracts light strongly and has a pleasant aromatic odour. Other bodies are also obtained at a higher temperature, but have not been investigated. The reaction seems to be $C_6H_5.COCl + C_2H_5I + Na_2 = NaI + NaCl + C_6H_5.CO.C_2H_5$. G. T. A.

Products of the Action of Fused Potash on Potassium Mesitylene Sulphonate. By O. Jacobsen (*Liebig's Annalen*, **195**, 265—292).—According to Fittig and Hoogewerff (*Annalen*, **150**, 333) the first product of the above reaction is oxymesitylenic acid, the xylenol being a secondary product. Biedermann and Ledoux (*Ber.*, **8**, 250) found, however, that the products of this reaction are mesitol and oxymesitylenic acid. The author concludes from the investigation of this reaction that mesitol is the chief product, and that oxymesitylenic acid is formed as a secondary product. The author finds that mesitol, $C_6H_2Me_3.OH$, melts at 68°, and boils at 219·5° (bar. 763 mm.), in its other properties it resembles the mesitol described by Biedermann and Ledoux (*loc. cit.*). Mesitol dissolves in concentrated sulphuric acid, yielding a sulphonic acid; this forms an easily soluble barium salt, crystallising in small needles. The sodium salt is also easily soluble in water and crystallises in flat prisms. Ferric chloride colours the aqueous solutions of these salts an intense blue.

Monobromomesitol is prepared by acting on mesitol dissolved in glacial acetic acid, with bromine in the cold. It crystallises from hot dilute alcohol in white, long, flexible, silky needles (m. p. 80°), and is identical with the compound described by Biedermann and Ledoux.

Dibromomesitol is formed by acting on the above derivative with bromine, or by dissolving mesitol in an excess of well cooled bromine. It is soluble in hot water, more easily in a hot aqueous solution of an alkaline carbonate, from which it separates on cooling. By crystallisation from alcohol, it is obtained in large, brittle, colourless prisms (m. p. 150°). It cannot be volatilised without decomposition. If the bromine used in the preparation of this body contains moisture, then a second compound is formed, which is the only product of the action when bromine acts on mesitol and water. This compound is more soluble in alcohol than dibromomesitol, crystallising in large acute golden-yellow rhombic plates, melting at 174° (corr. 176°), and subliming in shining golden-yellow leaflets. It is insoluble in water and in alkaline carbonates. It is decomposed by potash, forming a dark brown solution, from which, after acidifying with hydrochloric acid, ether extracts a new compound; this forms a semi-liquid mass becoming crystalline after some time. It is soluble in alcohol, yielding a dark brown solution, which is decolorised by sodium amalgam, but becomes brown again on exposure to air. This compound is

identical with Fittig and Hoogewerff's dibromoxylenol; its properties are, however, those of a quinone, and the author concludes from the analytical results that it is dibromometaxyloquinone, $C_8H_6O_2Br_2$.

Direct experiments with pure mesitol show that it is converted into oxymesitylenic acid by fusion with potash. Oxymesitylenic acid is sparingly soluble in hot water, crystallising from it in long six-sided, and from dilute alcohol in long, thin, flexible needles. It melts at 179° (according to Fittig at 176°). Its aqueous solutions give a blue coloration with ferric chloride.

The barium salt, $Ba(C_9H_9O_3)_2 + 5H_2O$, crystallises in thin rectangular plates or flat prisms often united to stellate groups. Heated to 110° it assumes a yellow colour, and at 140—150° becomes greyish; this is due to oxidation, as it may be heated without change to 180° in an atmosphere of hydrogen.

The calcium salt, $(C_9H_9O_3)_2Ca + 4H_2O$, is easily soluble, and crystallises in tufts of needles. At high temperatures, it behaves like the barium salt. The zinc salt, $(C_9H_9O_3)_2Zn + H_2O$, is less soluble in hot than in cold water; it crystallises in hard four-sided prisms.

The copper salt crystallises from its aqueous solutions in bright green silky needles; it is sparingly soluble in hot water; on heating the aqueous solution, a brownish-green basic salt separates out. $C_9H_9O_3K$ crystallises from concentrated aqueous solutions in long, glassy needles, united to form stellate groups. $C_9H_9O_3NH_4$ is very easily soluble in water, and crystallises in short quadratic prisms. At 100—110° it loses ammonia, also during the evaporation of its aqueous solutions. The aqueous solution of the ammonium salt gives a dark blue coloration with ferric chloride, and in concentrated solutions a blue precipitate; it also gives precipitates with solutions of copper, lead, mercuric, and silver salts.

The methyl salt, $C_9H_9O_3.CH_3$, is a colourless oil, having an aromatic odour, insoluble in water, but easily soluble in alcohol, and volatilised by a current of steam.

The author has already shown the constitution of oxymesitylenic acid to be: $C_6H_2(COOH)(OH)(CH_3)(CH_3) = [1.2.3.5]$ (this Journal, 1879, Abst., 247).

Biedermann and Ledoux found their oxymesitylenic acid to differ in some respects from that of Fittig and Hoogewerff. This difference the author shows to be due to the presence of an acid which is formed from the metaxylene contained in mesitylene prepared from acetone, and which is only obtained free from metaxylene with great difficulty. The barium salt of this acid is more easily soluble in water than barium oxymesitylenate, and may be separated from the latter by continued crystallisation from water. The acid gives a violet-blue coloration with ferric chloride, and melts between 116—120°. It is identical with the acid described by Engelhardt and Latschinoff (*Zeits. f. Chem.* 1869, 618), and shown by Schotten to be a mixture of para- and ortho-homosalicylic acids (Inaugural-Dissertation, Berlin, 1878, 36). Potassium mesitolsulphonate is easily resolved by fusion with potash into oxymesitylenic acid. The sulphonic acid from metaxylenol (1 : 3 : 4) (*Jacobsen Ber.*, **11**, 25), the barium salt of which is easily soluble in water, when fused with potash yields an oxytoluic acid

(m. p. 151°) (parahomosalicylic acid). This reaction is analogous to the decomposition of mesitolsulphonic acid, and since the oxidation takes place so easily, the author concludes that the methyl group situated between the OH and SO_3H groups is the one oxidised. Hence the constitution of the sulphonic acid is

$$C_6H_2(CH_3)(SO_3H)(CH_3)(OH) = [1:2:3:4].$$

Further, ethyldimethylbenzenesulphonic acid yields under similar conditions a monobasic oxyacid (*Ber.*, **7**, 1433). This acid differs from oxymesitylenic acid, since it melts at 147—149°, and is more soluble in alcohol than the latter, and crystallises from its alcoholic solutions in long needles. It is volatilised by steam, and ferric chloride colours its solutions blue. The constitutional formula of this oxyacid is $C_6H_2(COOH)(OH)(CH_3)(C_2H_5) = [1:2:3:5]$, and of the sulphonic acid $C_6H_2(CH_3)(SO_3H)(CH_3)(C_2H_5) = [1:2:3:5]$.

When mesitol or oxymesitylenic acid is fused with caustic potash, no trace of a phenol is formed, but oxidation takes place, resulting in the formation of oxytrimesitic and oxyuvitic acids. These acids are separated from oxymesitylenic acid by their non-volatilisation by steam, and from each other by the different solubilities of their barium salts, that of the latter being the more soluble.

Oxyuvitic acid, $C_6H_2(CH_3)(COOH)_2.OH$, crystallises from its aqueous solutions in colourless, branching needles; it is much more easily soluble in cold than in hot water. The aqueous solutions of the acid first prepared from its barium salt have a blue fluorescence, which is not the case with the acid prepared from its methyl salt. Its solutions give a cherry-red coloration with ferric chloride. The acid is soluble in alcohol and ether, but insoluble in chloroform and benzene. The acid appears to be decomposed by heat.

The sodium salt is very easily soluble in water; its concentrated solutions crystallise when surrounded by ice, in hydrated crystals which melt at the ordinary temperature. The cadmium salt is sparingly soluble in cold water, more easily in hot, from which it crystallises in stellate groups formed of needles or plates. With concentrated solutions of the sodium salt, ferric chloride gives a brownish-red precipitate, soluble in a large quantity of water, forming a red solution. Silver nitrate gives a gelatinous precipitate slightly soluble in hot water, easily soluble in ammonia, and becoming brown by continued boiling with water. With solutions of the free acid, silver nitrate produces a crystalline precipitate, easily soluble in hot water. Normal lead acetate gives with the sodium salt a crystalline precipitate, soluble in a large quantity of water; basic lead acetate, however, gives an amorphous precipitate, which is quite insoluble. Copper sulphate gives an apple-green precipitate, which dissolves in ammonia, forming a dark green solution.

Dimethyl oxyuvitate crystallises from hot alcoholic solutions in long needles, melting at 79°. It is insoluble in water, and is volatilised by steam. Böttinger (*Annalen*, **189**, 177 and 181) has already described the two oxyuvitic acids, the constitutional formulæ of which must be either $C_6H_2(CH_3)(COOH)(OH)(COOH) = [1:3:4:5]$ or

$C_6H_2(COOH)(COOH)(OH)(CH_3) = [1:3:4:5]$.

The acid prepared by the author, when heated at 200° with concentrated hydrochloric acid, yields a cresol, which by fusion with potash yields salicylic acid. Hence the latter of the above formulæ represents the constitution of the oxyuvitic acid prepared from mesitol.

P. P. B.

Molecular Weight of Indigo. By E. v. Sommaruga (*Liebig's Annalen*, **195**, 302—313).—Pure indigo prepared by Fritzsche's method (*J. pr. Chem.*, **28**, 139) was converted into vapour by immersion of the flask containing it in the vapour of boiling sulphur. The result gives the formula as $C_{16}H_{10}N_2O_2$. The same method has been applied to other bodies with good results. G. T. A.

Indigo-blue. By E. Schunck (*Chem. News*, **39**, 119—120, 129—130, 143—144).—In the first part of this paper reference is made to previous papers containing accounts of indigo-blue obtained from *Isatis tinctoria*, in which it exists in the form of a glucoside, indican: this, when treated with acids, splits up into indigo-blue and indiglucin. It is also decomposed by the action of caustic alkalis, a substance being formed which yields indigo-red, indifulvin, and leucine, when treated with acids. In some more recent experiments on indican from woad leaves, tyrosine has been found amongst the products of decomposition. The indican used consisted of a crude alcoholic extract of the leaves; it is therefore difficult to say whether the tyrosine existed ready formed in the leaves, or was the result of the decomposition of the indican; the latter is more probable, since tyrosine is almost insoluble in alcohol, and therefore would not be contained in the alcoholic extract in quantity. That there is some connection between indigo-blue and tyrosine is seen from the fact that tyrosine, $C_9H_{11}NO_3$, is indigo-blue, C_8H_5NO + 2 molecules of water, in which one atom of hydrogen is replaced by CH_3. Its formation may be explained by supposing indican to split up into tyrosine, indiglucin, acetic acid, and carbonic anhydride, $C_{26}H_{32}NO_{18} + 3H_2O = C_9H_{11}NO_3 + 2(C_6H_{10}O_5) + 2C_2H_4O_2 + CO_2$.

In order to ascertain whether other indigo-yielding plants contain indigo-blue in the form of a glucoside as in *Isatis tinctoria*, or in the free state, the following experiments were carried out:—

Polygonum tinctorium.—The leaves of this plant, which are large, oval, and glossy, and of a lively green colour, contain a large quantity of the colour-yielding substance. On cutting them in pieces and rubbing with water to a thin paste, filtering through calico, and separating the chlorophyll, albumin, &c., from the filtrate by precipitating with lead acetate, a liquid is obtained which yields indigo-blue on the addition of sulphuric or hydrochloric acid and allowing the mixture to stand for several hours. The isolation of the colour-yielding substance is effected by the method formerly employed to extract indican from *Isatis tinctoria*, or by the following, which is preferable:—The leaves are dried in a stove, and while still warm, ground to a powder, and exhausted with alcohol in a percolator. The alcoholic extract is evaporated at the ordinary temperature, and the residue freed from chlorophyll and other impurities by precipitation with lead acetate. On adding basic lead acetate to the filtrate, a primrose-yellow precipitate is

thrown down; this is washed with water and with alcohol, and finally suspended in absolute alcohol, and carbonic anhydride is passed through the mixture until the liquid assumes a yellow colour. On evaporating the filtrate at the ordinary temperature and adding water, a portion remains insoluble. This is separated by filtration, and the lead in the filtrate precipitated with sulphuretted hydrogen. The clear solution, evaporated at the ordinary temperature by means of a current of air, leaves a syrupy residue, from which the colour-yielding substance is obtained as a yellow syrup on treatment with absolute ether and evaporation. It shows no signs of crystallisation, is soluble in water, alcohol, and ether, the aqueous solution possessing a more or less acid reaction. It assumes a deep yellow colour when treated with caustic alkalis, and gives a light yellow precipitate with lead acetate. When it is mixed with sulphuric or hydrochloric acid, indigo-blue separates out, and the filtered solution gives the characteristic test for glucose with Fehling's solution. If, however, the aqueous solution is allowed to stand or is boiled, or mixed with caustic alkali and allowed to stand, no indigo-blue is deposited on addition of acid. In all probability the substance analogous to indican undergoes a molecular change, resulting in the formation of a body which yields indirubin and resinous matters on treatment with acids.

By allowing a large quantity of the aqueous solution to stand in contact with acids, indirubin and indifulvin are deposited, besides indigo-blue, showing that a portion of the substance undergoes some change, which in all probability may also take place in the cells of the leaf: for from leaves gathered late in the season a substance is obtained which, when treated with acids, yields far less indigo-blue and more indirubin and other products than the substance obtained from the younger leaves.

From these experiments it is inferred that the leaves of *Polygonum tinctorium* contain a substance identical with the indican from *Isatis tinctoria*, and also that no colouring matter exists ready formed in the healthy living plant.

If the leaves of *Polygonum tinctorium* be crushed, and after a short time plunged into boiling alcohol, the bruised portion assumes an intense blue colour, whilst the other portion becomes white.

If the leaves be immersed in water and the water frozen, the portion of the leaves which have been frozen appears of a dark colour after complete thawing, and after steeping in boiling alcohol they assume a dark-blue colour, whilst the unfrozen portions become white. The fresh leaves, after being plunged in cold alcohol or ether, and extraction of the chlorophyll, appear blue; this was supposed to prove the pre-existence of the free colouring-matter in the leaves; but by plunging them in boiling instead of cold alcohol, the colour-yielding substance is dissolved before it can decompose, and the leaves become of a pale yellow colour. Moreover, the alcoholic extract on evaporation does not deposit a trace of indigo-blue. The explanation offered for these phenomena is as follows:—The molecules of the glucoside, indican, are in a state of unstable equilibrium, and are enabled to preserve that equilibrium so long as they are contained in the cells of the living plant. As soon as that vitality ceases, the indican begins to decompose, and the molecules

arrange themselves as their chemical affinities predispose them; the result is, indigo-blue and indiglucin. This reaction takes place so rapidly that in some cases it would appear as if indigo-blue pre-existed in the living plant. By immersing freshly-cut sprigs of *Polygonum tinctorium* in dilute hydrochloric acid for some days, and exposing them to the air, the acid is rapidly absorbed by the stalk, passing first to the lower leaves and then to the upper. The absorption of the acid is attended with a change of colour from dark green to dirty yellow, and after some time to dark blue, commencing at the base of the leaf, and gradually extending to the apex, which is reached only in the case of the lower leaves. When the change of colour begins to appear in the upper leaves, they are immersed in hot alcohol, whereby the chlorophyll is dissolved, leaving those parts which have changed colour, blue, and the other portions white.

All these experiments were performed when the plants were in a state of vigorous growth.

The leaves of the *Polygonum tinctorium*, after developing the blue colour, present certain characteristic appearances.

(1.) The colouring matter is confined to the parenchyma of the leaves; the stem and ramifications in the coloured leaf may be traced as white veins on a coloured ground.

(2.) The younger leaves show more intense coloration, although probably all the leaves contain the same amount of colouring matter; but in the lower leaves it is more widely spread.

(3.) The colouring matter, when developed, is contained in the cells of the parenchyma in dots and parcels of various sizes, and in the amorphous state, the intensity of colour being determined by the crowding of the blue particles in the cells.

Bletia Tankervillæ.—Similar experiments, made with the leaves of the *Bletia Tankervillæ*, were attended with similar results, leading to the conclusion that these leaves contain a glucoside, similar to indican, which, on treatment with acids, yields a glucose and indigo-blue.

Indigofera tinctoria.—From want of material it was impossible to conduct experiments on this, the most important of all indigo-yielding plants; but according to P. Micheà, a glucoside exists in the indigofera of India, similar and in all probability identical with the indican from *Isatis tinctoria.*

From the following plants, supposed to yield indigo-blue, all attempts to obtain a body resembling indican have failed, and they show no indication of the presence of a colouring matter like indigo-blue. They are:—

Galega officinalis,
Hedysarum Onobrychis (sainfoin),
Polygonum Fagopyrum (buckwheat),
Polygonum Persicaria,
Rhinanthus Crista Galli,
Sophora japonica,
Spelanthes oleracea.

L. T. O'S.

Synthesis of Isatin. By L. Claisen and J. Shadwell (*Deut. Chem. Ges. Ber.*, **12**, 350—354).—The authors have succeeded in ob-

taining a body identical with the isatin of indigo by the following series of reactions:—Orthonitrobenzoic acid is treated with phosphorus pentachloride to obtain the corresponding chloride, $C_6H_4(NO_2).COCl$, and the latter is converted, by treatment with silver cyanide, into the cyanide, $C_6H_4(NO_2).CO.CN$, which, on prolonged contact with fuming hydrochloric acid, passes into the amide, $C_6H_4(NO_2).CO.CONH_2$. The amide is heated with potash, whereby it is converted into orthonitrophenylglyoxalic acid, $C_6H_4(NO_2).CO.COOH$, and this, by reduction with sodium amalgam or ferrous sulphate, yields isatic acid, $C_6H_4(NH_2).CO.COOH$. Finally, on treating the isatic acid thus obtained with hydrochloric acid, it is converted into isatin, $C_6H_4<\begin{matrix}NH\\CO\end{matrix}>CO$.

J. R.

Action of Phosphorus Pentachloride on Isatin and Allied Compounds. By A. Baeyer (*Deut. Chem. Ges. Ber.*, **12**, 456—461).—A chloride of isatin was described by the author in a former paper (this Journal, 1878, Abst., 884). It has now been obtained in crystals by acting on isatin with phosphorus pentachloride and benzene. It dissolves with a blue colour in ether, alcohol, acetic acid, and hot benzene. This chloride, C_8H_4ClNO, may be converted into indigo-blue by the action of acetic acid and zinc-dust and exposure to air for 24 hours, or better by mixing it with a solution of hydriodic acid in glacial acetic acid.

Indigo-purpurin is also formed when zinc-dust acts on isatin chloride, and may be precipitated from the solution by water and sodium carbonate. It dissolves in alcohol, &c., and when the alcoholic solution is diluted with water, it separates out in crystalline flocks; it crystallises from chloroform in tufts of needles. The absorption spectrum of its solutions is characteristic and quite different from that of indigo-blue. Indigo-purpurin is isomeric with indigo-blue, and identical with the body obtained by Baeyer and Emmerling from isatin by the action of acetic chloride, phosphorus trichloride, and phosphorus (*Ber.*, **3**, 514). It resembles indigo-blue in its general behaviour.

Chloroxindole chloride may be obtained by warming oxindole in quantities of 2 grams with three or four times as much pentachloride and a little oxychloride of phosphorus at 50—60°. The mass is dissolved in ether and shaken with water and levigated chalk. The ether is removed by evaporation and the residue distilled. The chloroxindole thus obtained has a penetrating smell somewhat resembling that of indole. It melts under boiling water, but may be heated to 103—104° in the dry state before it melts. It dissolves very sparingly in water, but easily in alcohol, &c. It has the formula $C_8H_5Cl_2N$, the chlorine taking the place of the hydroxyl in the side chains of dioxindole. It is characterised by its great stability. It is soluble in potash, but is reprecipitated unchanged on adding an acid. It has no basic properties. Although it is not attacked by sodium-amalgam, it may be reduced to indole by zinc-dust or iron filings and potash-solution. Hydriodic acid converts it not into indole, but into an amorphous colourless body, for which the name *retinindole* is proposed. This body has feeble basic properties, and is soluble in alcohol, but not in

soda solution. When heated, it yields an oil which thickens to a crystalline mass, having all the properties of indole. Two oxindoles are known belonging to the cinnamic acid series, carbostyrile and hydrocarbostyrile (*Zeits. f. Chem.*, 1869), and the latter of these corresponds perfectly with oxindole, yielding with PCl_5 a body convertible by sodium-amalgam into a non-volatile compound, which, when oxidised by chromic acid, yields a volatile basic oil, smelling like chinoline. This reaction establishes a connection between the quinine and indigo groups. G. T. A.

Tetramethylethylene and its Derivatives, and the Chemical Structure of Pinacone. By D. Pawlow (*Liebig's Annalen*, **196**, 122—128).—The description of tetramethylethylene and its derivatives, which is contained in this paper, has already appeared in other journals (*Ber.*, **11**, 513, and this Journal, 1878, Abst., 552). By the action of silver acetate on the bromide $C_6H_{12}Br_2$, an acetate was prepared, which, on saponification with baryta, yielded a crystalline glycol, $C_6H_{14}O_2.6H_2O$, melting at 46·3°, and identical with pinacone hydrate. From this pinacone would appear to be a tetramethylethylene glycol. W. C. W.

Constitution of Isodiphenic Acid and Fluoranthene. By R. Fittig and H. Lippmann (*Deut. Chem. Ges. Ber.*, **12**, 163—165). Isodiphenic acid, obtained by Fittig and Gebhard (*Ber.*, **10**, 2141), by fusing *diphenyleneketonecarbonic acid* with potash,

$$C_6H_4<\overset{CO}{\underset{\quad}{\quad}}>C_6H_3(CO_2H) + 2KOH = (CO_2K)C_6H_4.C_6H_4(CO_2K),$$

bears a great resemblance to diphenic acid, and like it, when heated with lime, yields *diphenyleneketone*, $C_6H_4<\overset{CO}{\underset{\quad}{\quad}}>C_6H_4$, together with a little diphenyl and carbonic anhydride. One carboxyl-group must therefore be in the ortho position with respect to the point of union of the two benzene nuclei.

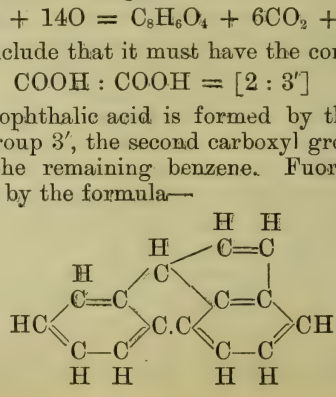
The authors now find that when *isodiphenic acid* is oxidised with potassium dichromate and sulphuric acid, it furnishes *isophthalic acid* in quantity agreeing with the equation—

$$C_{14}H_{10}O_4 + 14O = C_8H_6O_4 + 6CO_2 + 2H_2O,$$

from which they conclude that it must have the constitution

$$COOH : COOH = [2 : 3']$$

During oxidation, isophthalic acid is formed by the benzene nucleus with the carboxyl group 3′, the second carboxyl group being produced at the expense of the remaining benzene. Fuoranthene, therefore, must be represented by the formula—



Ch. B.

Vapour-densities of the three Isomeric Dinaphthyls. By WATSON SMITH (*Deut. Chem. Ges. Ber.*, **12**, 356).—The author has determined the vapour-densities of these isomerides by the method lately described by Victor Meyer (*Ber.*, **11**, 2253), the substances being heated in a lead-bath in an atmosphere of nitrogen. The results were as follows: $\alpha\alpha$-dinaphthyl, 8·67; $\beta\beta$-dinaphthyl, 8·73; $\alpha\beta$-dinaphthyl, 8·77. The theoretical density is 8·77. J. R.

Reduction of Anthraquinone-sulphonic Acids. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, **12**, 189—190).—The *sodium anthraquinone-monosulphonate* of commerce is nearly pure; other salts have been prepared from it by the author. When the sodium salt is boiled with red phosphorus and hydriodic acid of 1·7 sp. gr., it is converted into the moderately soluble soda salt of *anthracenehydride-monosulphonic acid*, $C_{14}H_{11}(SO_3Na) + \frac{1}{2}H_2O$. The barium, calcium, and lead salts are insoluble; the silver salt is soluble. Fusion with potash decomposes the acid, anthracene and anthracene-dihydride being given off. When boiled with sulphuric acid, hydrogen is given off, and *anthracene-disulphonic* acid formed. This sulphonic acid, treated in the way described in the previous paper, gave finally a mixture of anthraflavic and isoanthraflavic acids. The investigation is being continued. Ch. B.

Anthracene-derivatives of the Chrysazin Series. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, **12**, 182—188).—In a previous paper (*Ber.*, **11**, 1610) the author described two anthracene-disulphonic acids, obtained by the action of sulphuric acid on anthracene. One of these, distinguished as the β-acid, may be converted successively into $C_{14}H_8(OH)_2$, $C_{14}H_8(OAc)_2$, $C_{14}H_6O_2(OAc)_2$, and $C_{14}H_6O_2(OH)_2$, the last being *anthrarufin*, an isomeride of alizarin. In this paper he describes the similar compounds through which *α-anthracene-disulphonic acid* leads to *chrysazin*, another dihydroxyanthraquinone.

The sulphonic acids are best separated from sulphuric acid by the solubility of their lead salts in water; and from each other by the lesser solubility in water or soda solution of the sodium salt of the α-acid. Various compounds of both acids are described.

When fused with potash at a moderate temperature, these soda salts yield new acids, having the composition $C_{14}H_8(OH)SO_3H$. Heated with five times their weight of potash until the thick mass becomes liquid, they yield dihydroxyanthracenes, which may be separated by hydrochloric acid.

α-Dihydroxyanthracene, or *chrysazol*, $C_{14}H_8(OH)_2$, crystallises in plates, or in yellow, glistening needles, which decompose at 220°. It differs from all its known isomerides in being easily soluble in cold alcohol. Its properties correspond with those of a true phenol of the anthracene series, its solutions in alkalis becoming coloured by exposure to air. Its ammoniacal solution gives an orange-coloured precipitate with lead acetate. Ferric chloride or bromine strikes a blue-green colour with its alcoholic solution. Treated with acetic anhydride and sodic acetate it yields,

Diacetyl-chrysazol, $C_{14}H_8(OAc)_2$, melting at 184°, and this, when oxidised with chromic mixture, gives,

Diacetyl-chrysazin, $C_{14}H_6O_2(Ac)_2$, melting at 227—232°, and crystallising from acetic acid or alcohol in yellow needles, or thin yellow plates. This compound has also been obtained from chrysammic acid. By boiling with potash and precipitation with hydrochloric acid, it is converted into,

Chrysazin, $C_{14}H_6O_2(OH)_2$, which crystallises from alcohol in magnificent, yellowish-red needles (m. p. 191—192°). By sublimation, it forms red needles. It is soluble in alkalis and hot solutions of alkaline carbonates. Its calcium, barium, and lead compounds are insoluble. Its yellowish-red solution in strong sulphuric acid shows two weak absorption bands with the spectroscope, one in the green, and one between the green and blue. It is thus easily distinguished from anthrarufin.

It is in no respect different from chrysazin obtained from chrysammic acid (tetranitro-chrysazin), and is easily converted into this latter compound.

An isomeride of chrysammic acid, *tetranitro-anthrarufin*,

$$C_{14}H_2(NO_2)_4O_2(OH)_2,$$

is formed by boiling anthrarufin with fuming nitric acid. The two bodies and their salts (of which a few are described) are very similar. Ch. B.

Constitution of Phenanthrene. By G. Schultz (*Liebig's Annalen*, **196**, 1—32).—In support of the hypothesis of Fittig and Ostermayer (*Ber.*, **5**, 936) that phenanthrene is a di-ortho-compound, the author brings forward the following evidence:—1. That diiododiphenic acid, derived from Griess's diamidodiphenic acid, yields diphenic acid on reduction with sodium amalgam (*Ber.*, **11**, 215, and this Journal, 1878, Abst., 511). 2. That diamidodiphenic acid from diphenic acid is identical with Griess's metazoxybenzoic acid. Struve (*Ber.*, **10**, 75) regarded these acids as isomeric and not identical, since by distilling diamidodiphenic acid with soda-lime, he obtained, instead of benzidine, a base melting at 157.° The author, however, shows that Griess's acid yields a similar result if distilled with soda lime instead of baryta, but that when the barium salts of the two acids are distilled with baryta, benzidine will be formed in each case; hence he assumes the acids to be identical. When diamidodiphenic acid is heated to 170°, it partially melts, and is converted into a new amido acid (m. p. above 300°), which when heated with quicklime does not yield benzidine, but the base melting at 157.° W. C. W.

Phenanthrenequinone. By R. Anschütz and G. Schultz (*Liebig's Annalen*, **196**, 32—57).—Phenanthrene (b. p. 320—340°) obtained as a bye-product in the manufacture of anthraquinone from crude anthracene, was converted into phenanthraquinone by the action of a mixture of sulphuric acid, water, and potassium dichromate. The oxidation is carried on in large evaporating basins, at a gentle heat. The crude oxidation product, containing anthraquinone, phenanthrenequinone, phenanthrene diphenic acid, carbazol, acridine and diphenyleneketone, is dried, powdered, and digested for 12 hours with

strong sulphuric acid; water is added, and the mixture filtered. The residue is washed with water, and then with a cold dilute solution of soda, which dissolves out diphenic acid, and also a new acid, which forms a sparingly soluble barium salt. On exhausting the dried precipitate with ether, a mixture of phenanthrenequinone and anthraquinone remains. The phenanthrenequinone is dissolved out by a warm concentrated solution of acid sodium sulphite, and on the addition of potassium dichromate dissolved in dilute sulphuric acid to this liquid, the phenanthrenequinone is reprecipitated.

On distillation with dry soda lime, phenanthrenequinone is almost completely converted into diphenyl, but when the soda-lime contains a considerable amount of moisture, fluorene, fluorene alcohol, diphenylene ketone, and a red body are formed. The latter result is explained by the fact that the water and soda in the soda-lime convert the phenanthrenequinone into diphenyleneketone and diphenyleneglycollic acid, which decomposes, yielding fluorene alcohol. Heated with quicklime, phenanthrenequinone forms fluorene and diphenylene ketone.

In the same way when diphenic acid is distilled with quicklime, it yields diphenyleneketone, a red body, and traces of diphenyl, but when heated with a mixture of slaked and quicklime, it gives diphenylene ketone, diphenyl, and a red body, whilst with slaked lime, soda lime, or zinc-dust, diphenic acid yields diphenyl and a trace of the red body.

Alcoholic potash converts phenanthrenequinone into diphenic acid; alcoholic ammonia transforms it into *phenanthrenequinonimide*, crystallising in yellow needles (m. p. 167°). When it is heated in sealed tubes for several days with alcoholic ammonia, a mixture of several substances is obtained, one of which has the composition $C_{14}H_{10}N_2$, and is obtained in dark green or brown needle-shaped crystals, sparingly soluble in amyl alcohol.

The authors represent the constitution of phenanthrenequinone and its imide thus:—

$$\begin{array}{l} C_6H_4CO \\ \quad\quad\quad | \\ C_6H_4CO \end{array} \qquad\qquad \begin{array}{l} C_6H_4.CNH \\ \quad\quad\quad\quad | \\ C_6H_4.CO. \end{array}$$

W. C. W.

Action of Dehydrating Agents on Camphoric and Camphoramic Acids. By M. Ballo (*Deut. Chem. Ges. Ber.*, **12**, 324—329).—The author endeavoured to obtain the nitril of camphoric acid, $C_{10}H_{14}N_2$, by the action of dehydrating agents on the ammonium salts of these acids. Ammonium camphoramate was prepared by passing perfectly dry ammonia gas into a solution of camphoric anhydride in absolute alcohol. The attempt to obtain the nitril was only partially successful, because when the ammonium salts were heated with zinc chloride or syrupy phosphoric acid, the water present (or formed in the reaction) acted in such a manner as to regenerate camphoric acid, whilst the nitrogen was eliminated in the form of ammonia. It was only by treating ammonium camphoramate with phosphoric anhydride that he succeeded in obtaining a very small quantity of the nitril. In this case also a large quantity of camphoric acid was regenerated

by the action of the phosphoric acid produced in the reaction on the salt.

The nitril, which was obtained only in an impure state, was found to be a crystalline substance, smelling faintly of acetonitril, and subliming at 125—130°. It was soluble in alcohol and ether, but not in water.

Camphoric acid, when heated with dehydrating agents, is for the most part decomposed in the following manner: $C_8H_{14}(COOH)_2 = H_2O + CO + CO_2 + C_8H_{14}$, the chief product being the hydrocarbon C_8H_{14}, boiling at 122—126°, which the author calls *campholene*, and which he believes to be identical with the substance so named by Gille. But at the same time a small portion of the camphoric acid is decomposed in a different manner, resulting in the formation of another hydrocarbon, $C_{20}H_{32}$, boiling between 260° and 280°, to which the name *camphoterpene* is given.

In an experiment on the oxidation of Pfaundler's camphor chloride, $C_{10}H_{16}Cl_2$, with concentrated nitric acid, the author found the chief product to be camphoric acid, with a small quantity of an oily body having approximately the formula $C_{24}H_{35}ClO_3$. J. R.

Synthesis of Chinoline from Allylaniline. By W. Kœnigs (*Deut. Chem. Ges. Ber.*, **12**, 453).—When allylaniline vapour is passed over lead oxide at a low red heat, an oily distillate is obtained. This is mixed with dilute sulphuric acid, filtered, and the filtrate shaken up with ether. It is then heated with solution of potassium dichromate, the filtrate made alkaline and distilled in a current of steam. Chinoline passes over with the first drops of water. The formation of chinoline in this way corresponds with Baeyer and Caro's synthesis of indole from ethylaniline (*Ber.*, **10**, 692). G. T. A.

Nitro-chinoline. By W. Kœnigs (*Deut. Chem. Ges. Ber.*, **12**, 448—451).—When a solution of chinoline in concentrated nitric acid is gradually added to a mixture of 6 parts of fuming nitric acid with 10 of sulphuric acid, and heated on the water-bath, a body is obtained which has a composition intermediate between nitro-chinoline and nitro-lepidine, and probably consists of a mixture of the two. It is a powerful base, and is easily soluble in dilute acids. It dissolves sparingly in cold water, but is soluble in alcohol, ether, and more especially benzene. It forms a double platinum salt, crystallising in reddish-yellow needles.

On longer boiling with fuming nitric acid, chinoline yields an acid compound, possibly identical with Weidel's chinolic acid (*J. pr. Chem.*, **66**, 334).

On reduction, nitro-chinoline is converted into a compound (m. p. 71—74°) having approximately the formula of amido-lepidine. This body dissolves in dilute acids yielding a yellow solution. It is also soluble in water, and the solution becomes turbid on addition of strong caustic soda. It yields a platinum double salt. A tribromo-compound, as well as a sulphonic acid of chinoline have been described by Lubavin (*Annalen*, **155**, 311). G. T. A.

Decomposition of Tyrosine by Putrefaction. By T. v. Weyl (*Deut. Chem. Ges. Ber.*, **12**, 354).—The author finds that tyrosine, when digested with pancreatic fluid ("Pankeschlamm") in presence of water, yields a small quantity of a substituted phenol, probably paracresol. The amount of this product was found to be considerably greater when oxygen was excluded from the decomposing liquid.

J. R.

Oxidation of Quinine by Potassium Permanganate. By S. Hoogewerff and W. A. v. Dorp (*Deut. Chem. Ges. Ber.*, **12**, 158—161).—When quinine sulphate is oxidised at a boiling heat by potassium permanganate in alkaline solution (8·5—9·5 grams $KMnO_4$ to 16 grams dry quinine sulphate), from 22 to 26 per cent. of its carbon is obtained as oxalic acid, and from 41·2 to 43·4 per cent. of its nitrogen as ammonia. The resulting alkaline liquid contains, besides other nitrogenous bodies, about 15 per cent. (of the sulphate of quinine) of a tribasic acid, $C_8H_5NO_6$, probably *tricarbopyridenic acid*, $C_5H_2N(COOH)_3$. This acid retains $1\frac{1}{2}$ mols. of water of crystallisation at 100°, which it loses at 120°. It blackens at 190°, and melts at 244°. It is sparingly soluble in cold water, easily in hot water or alcohol, and almost insoluble in ether or benzene. Heated with lime in excess, it gives off the odour of the bases from Dippel's oil. The barium, calcium, silver, potassium, and copper salts of this acid are described.

Quinidine and cinchonine apparently yield the same acid. In many respects it resembles the acid similarly obtained by Ramsay and Dobbie (*Ber.*, **11**, 324), and named by them dicarbo-pyridenic acid.

Ch. B.

Solanine and the Products of its Decomposition. By A. Hilger (*Liebig's Annalen*, **195**, 317—325).—Previous papers on this subject are contained in *Liebig's Annalen*, **118**, 129; **123**, 341; **110**, 167; *Buchner's Repert. d. Pharm.*, **76**, 384; *Archiv. d. Pharm.*, **33**, 59; **116**, 114; *Zeit. f. Chem.*, 1866, 127.

The results of the author's analyses show that the composition of solanine may be expressed by the formula $C_{42}H_{87}NO_{15}$, that of solanidine by $C_{26}H_{41}NO_2$. The acetyl-compounds of those two bodies are acetyl-solanine, $C_{42}H_{69}Ac_6NO_{15}$, and acetyl solanidine, $C_{26}H_{36}Ac_5NO_2$. The author obtained 36 and 35·7 per cent. of glucose on resolution of solanine into solanidine, whilst according to Zwenger and Kind's equation—

$$C_{43}H_{69}NO_{16} + 3H_2O = C_{25}H_{39}NO + 3C_6H_{12}O_6,$$

it ought to yield 65·4 per cent. Further investigation is needed on this point.

G. T. A.

Sarracenia Purpurea. By F. Hétet (*Compt. rend.*, **88**, 185).—*Sarracenia purpurea*, a kind of pitcher-plant from North America, has for some time been used in rheumatic and gouty affections, and the author has found in it an alkaloïd identical in its character with veratrine. He has also confirmed the existence of an amine as recognised by Dragendorff, and has found, moreover, another alkaline substance soluble in water. The coincidence of the same therapeutic uses with the presence of the same active principle in the *Colchicaecæ* and *Sarracenia* is the more striking, as the two are in no way allied.

R. R.

Researches on Albumin. By Schützenberger (*Ann. Chim. Phys.*, [5], **16**, 289—419).—It having been observed that albuminoïd substances when submitted to the action of baryta under suitable conditions appear to be transformed entirely into crystallisable or into definite principles, it seemed reasonable to suppose that a carefully conducted and complete study of this reaction would be likely to materially contribute to a knowledge of the proximate composition of these bodies, if it did not ultimately solve the question respecting their constitution.

With this end in view, the author instituted and has carried out an extended series of experiments upon the action of baryta-solution at high temperatures on coagulated egg-albumin and other nitrogenous principles, the results of which investigation form the subject of the present memoir.

The albuminoïd under experiment was placed with the alkaline solution in an iron silver-lined autoclave, and heated to a definite temperature for some hours. After cooling, the contents of the cylinder, consisting of an amber-coloured liquid and a solid deposit, were transferred to a large flask, and the ammonia (1) distilled off into hydrochloric acid and estimated; the residue (2) in the flask was brought upon a weighed filter, washed with boiling water until the baryta was removed, then dried and weighed. The filtrate from the latter was precipitated by a current of carbonic anhydride, the barium carbonate removed, and the baryta remaining in the liquor exactly precipitated by sulphuric acid and its weight ascertained. The acid thus set free, which proved to be acetic acid (3) with traces of formic acid, was distilled off in a vacuum and again determined. The residue remaining from the distillation of the acetic acid, which the author terms *fixed residue* (4), is of a clear yellow colour, friable and easily removable from the vessel; it contains all the fixed principles such as leucine, tyrosine, &c., which are formed at the expense of the organic substance, in the proportions in which they are produced.

Determination of the Ammonia.—Having proved that coagulated albumin, washed with ether and dried at 140°, contained 16·5 per cent. of nitrogen, the effect of boiling it with three times it weight of baryta under ordinary pressure was ascertained. 1·2 per cent. of nitrogen was evolved in the form of ammonia within the first half hour, the disengagement proceeding slowly, until after 120 hours' boiling 2·2 per cent. had been eliminated: this number was never exceeded. At 120° in the autoclave, 2·2 per cent. of nitrogen was evolved by digestion during six or eight hours; at 150°, with only twice its weight of baryta, 3·1 per cent. was obtained; whilst between 150° and 180°, with three parts of baryta for 24 hours, 3·95 per cent. was disengaged, and the limit of 4·0 per cent. was not exceeded even by heating with six parts of baryta for six or eight days. These three limits indicate clearly three successive and different stages of decomposition.

Insoluble Barium Salts.—The quantity of this deposit like the ammonia varies with the temperature and with the proportion of baryta used: in composition as well as in weight, it undoubtedly bears a direct relation to the quantity of ammoniacal nitrogen disengaged. It consists mainly of barium carbonate and oxalate, with a certain amount of

barium phosphate and sulphate; the proportions of the two former, the only important elements in the mixture, were as follows: From 100 grams of albumin—

			N.	$BaCO_3$.	BaC_2O_4.
With 200 grams of	BaH_2O_2	at 100°	2·1	3·6	3·4
,, ,,	,,	at 120	2·3	4·7	4·3
,, ,,	,,	at 150	3·1	10·5	5·0
,, 300 grams	,,	at 180	4·0	10·8	8·0
,, ,,	,,	at 200	3·95	11·0	8·6
,, 600 grams	,,	at 180	3·79	11·2	18·2
,, ,,	,,	at 250	4·41	12·5	24·2

Acetic Acid.—The proportion of this acid is always relatively small, it varies with the temperature and the proportion of the baryta as in the previous instances, the smallest quantity obtained being 2·7 per cent., and the greatest 5·4 per cent.

Fixed Residue.—The total weight of this residue, obtained as before mentioned (including 6·53 per cent. of organic matter carried down by the barium carbonate), amounted in one experiment to 95·83 per cent., and in another to 96·5 per cent. of the albumin used; it is evident therefore that the decomposition under the influence of baryta is accompanied by a fixation of the elements of water, inasmuch as the separate weights of the components being added together, there is always an excess varying from 10 to 14 per cent. The ultimate analyses of the fixed residue gave very constant numbers, which did not vary greatly even under different formative conditions, the mean numbers being C = 48·16; H = 8·2; N = 11·03; O = 30·75 per cent.

Volatile Oil.—There is formed, during the decomposition of albumin in the manner under discussion, a very small quantity of a volatile oil, about 1 or 2 per cent., which could not be obtained in sufficient quantity for analysis under ordinary conditions. An operation on the large scale with 10 kilograms of albumin enabled about 50 or 60 grams of the oil to be collected and an examination to be made. It had no fixed boiling point; on account of the small quantity at disposal, it was not possible to separate its constituents by fractional distillation: it was therefore divided into four portions boiling from 113° to 120°; 120° to 140°; 140° to 180°; and above 180°, and an analysis of each portion made. From the results of these analyses the author is of opinion that the oil is a mixture of two substances, one, the more volatile, containing oxygen but not nitrogen; the other, nitrogen but not oxygen. The presence of pyrrol in the oil was clearly established by means of its well-marked reactions. The formula, $C_{16}H_{23}NO_3$, calculates very nearly to the percentage obtained, from which if the formula of pyrrol be deducted (C_4H_5N) there remains $3(C_4H_6O)$, which may be considered to represent approximately the composition of the remainder. A small quantity of a sulphuretted body is also contained in the oil. The quantity of this albuminol obtainable is so small that it is impossible to assign to it any important part in the constitution, or in the reactions representing the decomposition of albumin.

The proximate analysis of the fixed residue was a work of very great difficulty, and every method that could be devised was tried with only

partial success. It was eventually found that the best method was to treat the residue with neutral solvents, and to separate the constituents as far as possible by means of fractional crystallisation. The identification of the various principles was afterwards effected by means of ultimate analysis, which, in the absence of any well characterised reactions, was found to be the only sure or practicable means of arriving at satisfactory results. More than 500 combustions were thus made.

The two terms which were the easiest to isolate from the fixed residue, on account of their slight solubility, were *tyrosine* and *leucine*, the former, which is produced to an extent varying from 2·3 to 3·5 per cent., was recognised by its crystalline form, and by its well-known colour reaction with mercurous nitrate; the latter was also obtained in a well-crystallised condition, and gave results on analysis agreeing accurately with the formula $C_6H_{13}NO_2$.

The successive crystalline deposits, obtained by progressively concentrating the solutions from which the leucine, &c., had been partially separated, were composed of amido-valeric and amido-butyric acids, together with two new, definite, crystallisable products, *tyroleucine* $C_7H_{11}NO_2(C_nH_{2n-3}NO_2)$ and a body corresponding with the formula $C_6H_{11}NO_2(C_nH_{2n-1}NO_2)$: the quantity of tyroleucine obtained was about 60 or 70 grams from 10 kilograms of albumin. Tyroleucine presents itself as a white crystalline deposit of chalky aspect, possessing scarcely any taste, but soluble in about 20 parts of water at 15°. It melts and decomposes at 240°, breaking up into a white sublimate and a volatile oily base having an odour of raddish; it leaves behind an abundant yellow vitreous residue. The analysis of the chloroplatinate of the base gives it the formula of collidine, $C_8H_{11}N$, and of the vitreous residue the formula $C_{14}H_{18}N_2O_2$; the decomposition of tyroleucine may therefore be taken as proceeding thus—

$$2(C_7H_{11}NO_2) = C_{14}H_{18}N_2O_2 + 2H_2O$$
$$2(C_7H_{11}NO_2) = CO_2 + \underbrace{C_8H_{11}N}_{\text{Collidine.}} + \underbrace{C_5H_{11}NO_2}_{\text{Amido-valeric acid.}}$$

from which one is led to suppose tyroleucine to be a compound of amido-valeric acid with a body of the formula $C_9H_{11}NO_2$, the latter differing from tyrosine only by an atom of oxygen. This is rendered more probable by the fact that tyrosine, when heated under similar conditions, breaks up into CO_2 and a base, $C_8H_{11}NO$, which differs from collidine only by an atom of oxygen.

Among the homologues of leucine, amido-valeric and amido-butyric acids were met with in quantity, but amido-propionic acid in very small proportion only; its presence, however, was clearly and distinctly made out.

To the compounds of the formula $C_nH_{2n+2}NO_2$, the author gives the generic name *leucines*, and to those of the formula $C_nH_{2n-1}NO_2$ the names *leuceïnes* ($n = 6$); both seem to be frequently produced by the splitting up on crystallisation of bodies of the formula $C_mH_{2m}N_2O_4$ ($m = 10$ or 12); however by repeated fractional crystallisation the

compound $C_{12}H_{24}N_2O_4$ gave always the same analytical numbers, from which it is fair to suppose that it has an independent existence. The supposition is moreover strengthened by the fact that similar results were obtained with the lower homologues containing 11, 10, 9, and even 7 atoms of carbon.

For these latter bodies, the name *glucoproteins* has been adopted, on account of their sweet taste; they crystallise less easily than the leucines, especially the lower terms; they are very soluble in water, but almost insoluble in cold absolute alcohol; hot alcohol of 90 per cent. however dissolves them with ease.

Another substance resulting from the decomposition of albumin, which is produced in important quantity, is a yellow viscous body obtained by precipitating certain mother-liquors from which leucines have been crystallised by ether. Dried at 120°, it is converted into a transparent amorphous mass, which on analysis gives numbers comprised between the formulæ $C_5H_9NO_2$ and $C_4H_7NO_2$, very often sensibly approximating to the formula $C_9H_{16}N_2O_4$; it appears in fact to be constituted in great part of butyric leucine with an admixture of some superior homologue.

The longer the action of baryta on albumin is continued, and the more concentrated the solution, the greater is the proportion of leucines and of leuceïnes formed, whilst under the contrary conditions, the intermediate bodies, or glucoproteins, constitute the bulk of the fixed residue, representing the initial terms of the hydration of albumin; under all circumstances caproic leucine and tyrosine appear to be the ultimate terms of the decomposition.

The mechanism of the reaction would therefore appear to admit of the following explanation. The albuminoïd molecule losing ammonia and carbon as carbonic, oxalic, and acetic acids, and assimilating water, is converted into a comparatively simple mixture of glucoproteins, $C_nH_{2n}N_2O_4$, containing as its principle term $C_9H_{18}N_2O_4$: by the prolonged action of baryta and a high temperature, these glucoproteins split up partly into leucines and leuceïnes, and partly into double compounds formed by the union of glucoproteins and leuceïnes with the leucines.

The leuceïnes may perhaps be regarded as amido-acids of the acrylic, or of an isomeric series. They reduce ammoniacal silver nitrate on warming, and are attacked by bromine in the cold with formation of HBr and an acid of formula $C_nH_{2n-1}NO_3$. In the analysis of the fixed residue, the ratio of nitrogen to oxygen is never rigorously 1 : 2, but there is always a slight excess of oxygen, so that the ratio is nearer 1 : 2·1 or 1 : 2·3; this difference indicating the presence of small quantities of non-nitrogenous compounds, or of bodies in which the atomic relation of nitrogen to oxygen is greater than 1 : 2. A careful examination for such bodies among the crystalline deposits resulted in the detection of a few grams of an acid from 1 kilogram of albumin, offering a composition very close to that of *glutamic acid*, $C_5H_9NO_4$, and a smaller quantity of a second, whose composition was that of glutamic acid minus water, $C_5H_7NO_3$, which has been called *glutimic acid*. Judging from their amount, these acids play but a secondary part in the constitution of the mixture resulting from the decomposition of albumin: the acids, on the other hand, which are capable of being extracted in reasonable

quantity from the insoluble barium salts, do not exhibit a constant composition; they appear to be residues of a progressive decomposition, and to be susceptible of being resolved by the continued action of baryta into a mixture of leucines and oxalic acid.

Without following all the steps by which the author succeeded in tracing the presence of the various bodies which are met with in small proportions as constituents of the fixed residue, and modify slightly the ratio between the nitrogen and oxygen, we may sum them up as follows:—1. Traces of succinic and lactic acids. 2. Tyrosine. 3. Amido-acids of the type of $C_nH_{2n-1}NO_3$ glutamic and aspartic acids. 4. Amido-acids of the type $C_nH_{2n-3} = NO_3$ glutimic acid. 5. Amido-acids of the types $C_mH_{2m-4}N_2O_6$ and $C_nH_{2n-1}NO_3$. 6. Intermediate compounds of the type $C_mH_{2m}N_2O_5$.

The principle, which is the most constant among the products of the decomposition, and whose proportion is the most easy to determine on account of its sparing solubility, is tyrosine. The maximum quantity obtained of this body was 3·5 per cent.; if, therefore, one molecule of albumin reacts in the formation of one molecule of tyrosine, it points to the approximate molecular weight 5,500 for the former, since $\frac{181}{5,500} = 3{\cdot}3$. An expression of the form $C_{240}H_{387}N_{65}O_{75}S_3$ corresponds with a molecular weight equal to 5,473, which satisfies the conditions involved in the determination of the sulphur and tyrosine, as well as the results of elementary analysis, thus—

	C.	H.	N.	O.	S.	Mol. weight.
Experiment..	52·57	7·16	16·6	21·8	1·8	—
Theory.....	52·62	7·07	16·62	21·94	1·75	5,473

Again, taking as the basis of calculation the experiments made with 5 or 6 parts of baryta at 180°, the centesimal proportions of the products were—

N as NH_3.	$BaCO_3$.	BaC_2O_4.	$H_4C_2O_2$.
4·03	17·6	11·0	4·6

which corresponds very fairly for 5,473 parts of albumin with—

NH_3.	$H_2C_2O_4$.	CO_2.	$H_4C_2O_2$.
16 mols.	4 mols.	3 mols.	4 mols.

From these numbers the following equation may be written, which moreover would give a fixed residue of 99·6 per cent.:—

$$C_{240}H_{387}N_{65}O_{75}S_3 + 60H_2O = 16NH_3 + 4C_2H_2O_4 + 3CO_2 + 4C_2H_4O_2 + C_{221}H_{435}N_{49}O_{105} + S_3.$$

Deducting a molecule of tyrosine from the formula of the fixed residue, we have $C_{212}H_{424}N_{48}O_{102}$, which approximates very closely to an expression of the form $C_nH_{2n}NO_2$, differing from it only by a slight excess of oxygen.

By taking in this manner the series of experiments made with different proportions of baryta and at different temperatures, a number

of equations may be written, in all of which the theoretical composition of the fixed residue corresponds very closely with that obtained experimentally.

There can be no doubt that, during the hydration of albumin, as many molecules of water are assimilated as there are molecules of ammonia liberated; if then from the proposed formula for albumin we deduct the ammonia, carbonic, oxalic, and acetic acids in the proportion furnished by experiment, less a number of molecules of water equal to the number of molecules of ammonia (adding as many molecules of water as there are molecules of carbonic anhydride produced, since the latter probably results from the decomposition of urea) we shall have—

$$[16NH_3 + 4C_2H_2O_4 + 3CO_2 + 4C_2H_4O_2 - 16N_2O + 3H_2O],$$

which leaves $C_{221}H_{341}N_{49}O_{581}$, an expression which corresponds with the type $C_nH_{2n-2}NO$ quite as nearly as that of the fixed residue with the type $C_nH_{2n}NO_2$, the difference on both sides being a slight excess of oxygen. The molecule of albumin therefore resembles that of a body whose formula is $x(C_mH_{2m-4}N_2O_4)$, where $m = 2n$, and undergoes hydration in two distinct steps. At 100°, with a limited proportion of baryta, the grouping fixes a number of molecules of water equal to one-half the number of atoms of nitrogen which it contains, and becomes $x(C_mH_{2m-2}N_2O_3)$. The latter, at a higher temperature, can in its turn fix a number of molecules of water equal to the number of atoms of nitrogen which it contains, changing itself to the formula $x(C_mH_{2m}N_2O_4)$, the final result being the assimilation of as many molecules of water as the albumin contains atoms of nitrogen. *Albumin is then probably an imido-derivative, which by hydration changes into a mixture of amido-derivatives.*

To return to the observed relation between the ammoniacal nitrogen evolved, and the carbonic and oxalic acids produced, it is noticeable that two molecules of ammonia are disengaged for each molecule of acid generated; the simplest reaction which could account for such a phenomenon would be to suppose that the ammonia results from the hydration of urea or cyanamide and oxamide, a supposition which acquires a much greater degree of probability when it is shown that a very large majority of animal nitrogenous principles, when similarly decomposed, yield a quantity of ammonia which is precisely the amount that should be furnished by the carbonic and oxalic acids produced at the same time, supposing the whole to result from the reaction above mentioned. The author has examined wool, hair, ossein, isinglass, gelatin, goat's hair, silk, fibrin, and chondrin, in all of which the above relations held good.

Summary.—It has been shown: 1. That the mixture of fixed principles derived from albumin by hydration contains only amido-derivatives. 2. That these derivatives can be divided into two unequal portions, one, the weight of which is about 16 to 18 per cent., containing the substances in which the ratio of nitrogen is 1 : 3, or 1 : 4, or 2 : 5; the most important fraction of this portion consists of acids of the formula $C_nH_{2n-1}NO_4$, C_nH_{2n-3}, $NO_3C_{2n}H_{4n-4}N_2O_6$, and $C_nH_{2n-1}NO_3$, the intermediate term being only a molecular combination of the terms

$C_nH_{2n-3}NO_3$ and $C_nH_{2n-1}NO_3$. The second portion, which constitutes $\frac{4}{5}$ths of the residue, may be represented by the formula $x(C_nH_{2n}N_2O_4)$ with a value for n a little less than 9. According as the limit of hydration is attained, the products formed belonging to the type $C_mH_{2m}N_2O_4$ (where m is a multiple of n) are progressively resolved into simple bodies belonging to the same apparent type; these again are resolved into bodies of the type $C_nH_{2n}N_2O_4$, which in their turn are resolved into leucines, $C_nH_{2n+1}NO_2$, and leuceïnes, $C_nH_{2n-1}NO_2$. This interpretation is not affected by the presence of more highly oxygenated acids in the fixed residue, since they may be considered as derived from any of these bodies by substitution of O for H_2.

To the memoir is added an appendix, in which are given the results of some analyses made of fixed residues obtained from different sources. Albumin purified by Wurtz's method was substituted for crude albumin; the baryta was precipitated in one instance by carbonic anhydride, in another by carbonic anhydride and sulphuric acid, and in a third by carbonic anhydride, ammonia, and ammonium carbonate, but no important differences were observable in the products of decomposition. It was also found to be a matter of indifference whether the hydration of the albumin was begun by the action of other agents less energetic than baryta, such as dilute sulphuric acid; on completing the action by the intervention of baryta as usual, the same result was obtained as in the previous instances. A fixed residue obtained by the action of baryta was subsequently boiled for 24 hours with a 20 per cent. sulphuric acid, but its composition was not found to be sensibly affected.

In a final operation, conducted with the usual reagents, the action of baryta upon albumin was carried to its extreme limit. The fixed residue was carefully examined to see whether any substance was produced under such condition, which had not been found, or had been overlooked in previous experiments: nothing however was met with but the usual mixture of leucines and leucëines.

The molecular weight of the various glucoproteins still remains to be determined. J. W.

Physiological Chemistry.

Transformation of Glycogen by the Salivary and Pancreatic Ferments. By J. Seegen (*Pflüger's Archiv. f. Physiol.*, **19**, 106—128).—This research was begun with a view of ascertaining the difference in behaviour towards diastatic ferments of glycogen derived from the liver of dogs fed on a meat, and on a bread and potato diet respectively. The author found that the behaviour of the two glycogens was identical. Further experiments, made partly in conjunction with Dr. Kratschmer, lead him to the following conclusions:—

(1.) Glycogen is not entirely converted into sugar by saliva and by pancreas extract; only 60 to 70 per cent. of the glycogen is thus

transformed. (The author estimated the sugar by causing it to enter into combination with potash.)

(2.) The sugar formed is not grape-sugar, for it possesses considerably less reducing power and a much higher specific rotation. The former is 66 per cent. of that of grape-sugar, and the specific rotation ranges between 120° and 130°.

(3.) Diastase acts similarly to saliva and pancreas extract.

(4.) The above ferments do not transform starch entirely into sugar. The sugar formed also possesses less reducing and a higher rotatory power.

(5.) The sugars formed by ferments from starch and glycogen, the author terms ferment-sugars.

(6.) Boiling with acids converts about 75 per cent. of glycogen into grape-sugar. Complete transformation of the glycogen into sugar occurs only when the glycogenic solution is heated in closed tubes at 100° C. for 36 or 48 hours.

(7.) The sugar formed in the liver is grape-sugar.

(8.) The author distinguishes two varieties of dextrin which are also products of the action of the ferments:—(*a.*) Brücke's achroodextrin precipitated by weak alcohol, and which is further transformed into sugar by the ferment. (*b.*) A second form, which is only very slightly soluble in alcohol of 90 per cent., and *cannot* be further transformed into sugar by the action of ferments. The author terms this *dystropodextrin* (δυστροπος = obstinate, tough). E. C. B.

Formation of Emulsion, and the Influence of the Bile in Digestion. By G. Quincke (*Pflüger's Archiv. f. Phys.*, **19**, 129—144).—The author's chief results are as follows:—

Soap-solution diffuses itself on the limiting surface between fatty oils and water or aqueous saline solutions.

This diffusion gives rise to rotatory movements in the interior of the oil and of the surrounding fluid, small drops of oil becoming at the same time detached.

Portions of soap, so small as to be unrecognizable by the microscope or otherwise, suffice to produce this diffusion and these movements.

In a weak solution of soda, fatty oils containing free fatty acids form hard soap, which dissolves in the surrounding fluid and diffuses itself on the surface.

With a certain concentration of the soda-solution and a certain solubility of the soap produced, the diffusion is repeated at definite periods, and separates a great quantity of small drops of oil. This explains the spontaneous emulsification and the amœboid movements of oil-drops in a dilute solution of soda described by J. Gad.

The drops of oil are coated by a thin layer of soap, which prevents the drops from running together, and materially increases the durability of the emulsion.

This spontaneous emulsification does not occur with castor-oil, as the soaps formed from it by contact with a solution of soda are too soluble.

Bile, by facilitating the solution of the hard soaps, can assist in the emulsification of the intestinal contents, or under certain circum-

stances it may retard the same. It increases the mobility of the surface of the oil.

Froth is an emulsion with air instead of oil. Its durability depends on the same physical conditions as the durability of oil-emulsions. E. C. B.

Nature of the Albumins in Hydrocele. By J. Béchamp (*Compt. rend.*, **88**, 608—610).—In a former communication published in *Compt. rend.*, **87**, the author had shown that in all hydroceles, the liquid contains an albuminous matter having a lævogyratory power of 70°. In the present paper he states that he has succeeded in separating from this albuminous matter two, if not three distinct albumins. Of these one has a rotatory power of 65·8°, another of 72·2°. The first is precipitated by monoplumbic acetate, and has no action on starch; the second is precipitated by hexplumbic acetate, and renders starch soluble after acting on it for one or two hours at 40°. They both differ from the albumin of the blood, for the highest rotatory power of any of the blood-albumins does not exceed 63°; moreover, the albumins of blood are absolutely insoluble in water after their precipitation by alcohol, whilst those of hydrocele, on the contrary, are soluble. The author has never found the albumins of the blood in the liquids of discharges. In such cases, therefore, there is, not merely a transudation, but a transformation. R. R.

Composition of Mare's Milk. By M. Schrodt (*Landw. Versuchs-Stat.*, **23**, 311—316).—The author analysed the milk of a five years old mare, ten weeks after foaling, with the following results:—

Dry substance	8·85	per cent.	
Ash	0·37	„	
Fat	1·27	„	= 8·89
Albuminoïds	1·50	„	
Milk sugar.....	5·75	„	

The fresh milk was perfectly neutral. J. R.

Chemistry of Vegetable Physiology and Agriculture.

On Alcoholic Fermentation. By P. Schützenberger and A. Destrem (*Compt. rend.*, **88**, 593—595).—This paper is a continuation of the researches described in *Compt. rend.*, **88**, 287, and this vol., p. 476. 100 grams of fresh *unwashed* yeast containing 1·9 gram of nitrogen as insoluble albuminoïds, contained only 1·1 gram of nitrogen after decomposing 200 grams of sugar, whilst after maceration in water only, under the same conditions, there remained 1·5 gram of nitrogen. The total weight of the insoluble part of the yeast diminished less than by maceration only; and in experiments with small quantities of yeast, even increased, as in Pasteur's experiments.

Washed yeast, even in the absence of air, also decomposes sugar rapidly enough, 100 grams of yeast causing 200 grams of sugar to disappear in 24 hours. But the weight of insoluble residue diminishes about 40 per cent., and very much more than by simple maceration.

100 grams of fresh *washed* yeast containing 19—20 grams insoluble matter, furnished only 11·8—13·2 grams after decomposing 200 grams of sugar, whilst after simple digestion with water it still furnished 15·8—16 grams.

The loss is due to the transformation of albuminoïd matter into soluble amidated compounds. The 19 grams of original insoluble yeast contained 1·9 gram nitrogen; the 11·8 grams left after fermentation contained only 0·57 gram of nitrogen: 1·33 gram of nitrogen was therefore eliminated by solution of the proteïd matters. Since these contain about 16 per cent. of nitrogen, 1·33 gram of nitrogen = 8·3 grams albuminoïd matter, and 19·0 − 8·3 = 11·7, the weight of the residual yeast. Another experiment cited gives a similar result.

100 grams of fresh washed yeast corresponding with 18·4 grams of insoluble matter containing 1·895 gram of nitrogen, gave, after simple digestion, 15·84 grams insoluble residue containing 1·71 gram nitrogen. The loss in nitrogen is 0·185 gram, equivalent to 1·1 gram albuminoïd matter. The total loss is 2·6 grams; 2·6 − 1·1 = 1·5 gram non-nitrogenous matter eliminated by secondary fermentation.

100 grams of fresh washed yeast, by fermentation with access of air, lost only 3·2 grams proteïd matter, and fixed 4·84 grams non-nitrogenous matter, the weight of insoluble residue increasing from 18·4 grams to 20·04 grams.

Conclusions.—(1.) Yeast, placed under conditions which prevent its multiplication and development, nevertheless retains the power of decomposing sugar, and in so doing it loses more nitrogen than when simply digested with water deprived of sugar and oxygen. The proportion between the quantity of sugar decomposed and the new yeast formed, *i.e.*, the fermenting power, thus becomes a *negative* quantity. (2.) The proximate composition of yeast, or the proportion between its albuminoïd and non-nitrogenous constituents, varies with the composition of the medium in which it lives.

The authors have previously recognised the formation of *aldehyde* in fermentation conducted without the presence of air. The aldehyde found in wine, &c., is therefore not due solely to oxidation of the alcohol. Its formation is directly connected with the decomposition of sugar, and may perhaps accompany the production of 6 molecules of glycerin to 1 of succinic acid, the sum of which ($=C_{22}H_{54}O_{22}$) contains more hydrogen than the original sugar. J. M. H. M.

Formation of Starch in Chlorophyll-grains in Absence of Light. By J. Böhm (*Versuchs-Stat.*, **23**, 123—156).—This paper contains details of a series of experiments on the above subject made with the germinal plants of the scarlet-runner; in some cases parts of the leaves were excluded from light, and in other cases the entire plants. The experiments appear to show that light is not necessary for the formation of starch. P. P. B.

Analysis of some Fodders, and Observations on the Damage caused to Italian Beans by the Bean Insect (*Bruchus rufimanus, Sch.*). By H. Grosjean (*Compt. rend.*, **88**, 600—602).—The samples of horse food analysed comprise three samples of oats from different provinces, crushed maize, horse-beans (Italian beans), wheat bran, hay, chaff, and a food composed of oats, maize, and beans, already mixed.

Pectic bodies were estimated by Schlœsing's method. The oats contained 0·20—0·37 per cent.; the maize only traces; the chaff, bran, and hay 1·00, 2·03, and 4·46 per cent. respectively; the beans 1·88 per cent. as pectate of lime, which is contained in the integument of the bean. This integument, forming 0·16 of the total weight of the seed, is removed in the manufacture of bean flour, and is found in commerce under the name of bean bran (*son de fèves*) containing 11·5 per cent. of pectic bodies.

Sugars.—The seeds and bran may be considered to contain cane-sugar, whilst the hay and chaff probably contain glucose. The percentages are, oats, 0·5—1·0; maize, 0·8; beans, 1·25; bran, 2·5; hay, 1·5; chaff, traces.

Fifty per cent. of the beans were attacked by the *Bruchus rufimanus*, and the average number of insects to each bean was two, so that the sample contained *as many insects as beans.* The attacked beans when weighed against the sound ones showed a loss of 18·5 per cent., or nearly *one-fifth.* The perfect insects contained in 100 parts, 50 of water, 15·8 of fatty matter, and 5·5 of nitrogen. Each *Bruchus* consumes on an average 140 mgrms. of the bean, containing 37 mgrms. of albuminoïd matter, 2·4 mgrms. of fatty matter, 55·4 mgrms. of starch, and 1·8 mgrm. of sugar. Of these materials the insect fixes 1·8 mgrm. and loses 0·6 mgrm. of fatty matter, and eliminates about nine-tenths of the nitrogen which it consumes. J. M. H. M.

Absorption Power of Soils. By J. M. v. Bemmelen (*Landw. Versuchs-Stat.*, **23**, 265—320).—This is a continuation of a previous paper (*ibid.*, **21**, 135; *Chem. Soc. J.*, **34**, 598). The authors principal results are summed up as follows:—

Soils absorb alkali from hydrates of the alkalis and alkaline earths, and from salts of weak acids (borates, carbonates, phosphates, &c., which are more or less dissociated in aqueous solution), but without exchange of bases, the free hydrated silica in the soil taking up alkali, whilst (in the case of salts) a corresponding quantity of acid alkali-salt is formed.

When the basic silicates (and humates) in a soil are decomposed by boiling it with strong hydrochloric acid, and the bases are removed by washing, so that only acid aluminium silicates, quartz, the separated silica, and humus residues are left, the absorption of alkali or alkaline earth from salts of strong acids almost ceases. But, on the contrary, the absorption of alkali from salts of weak acids (borates, carbonates, phosphates) is increased. The free silica resulting from the decomposition of the basic silicates takes up free (dissociated) alkali in the saline solution, whereupon a fresh quantity of free alkali is produced by dissociation and is taken up in turn, and this process goes on until an equilibrium is established between the amount of

silica, the amount of acid and neutral salts in solution, and the volume of water present at the prevailing temperature.

A soil whose power of absorbing alkalis and alkaline earths from salts of strong acids has been destroyed by boiling with strong hydrochloric acid, does not recover this power on simply mixing with it another salt of a strong acid, such as calcium chloride or sulphate. But the absorption power is restored when the soil is mixed with alkali-salts of weak acids. When, for instance, the soil is mixed with calcium carbonate, and then treated with solution of potassium chloride, the following reactions take place. The potassium chloride solution first dissolves a little calcium carbonate, so that calcium chloride and potassium carbonate are formed. Half the potash of the latter is then taken up by the hydrated silica of the soil, the other half forming acid carbonate. Equilibrium between the salts in solution is thus disturbed, and the same process is repeated until ultimately equilibrium is established between the combining power of the silica, the solvent power of the water present, and the chemical affinities of the salts $CaCl_2$, $CaH_2(CO_3)_2$, $CaCO_3$, KCl, and $KHCO_3$.

When a soil which has been boiled with strong hydrochloric acid is boiled with saline solutions, its hydrated silica acts to some extent upon the latter, forming a greater or less quantity of silicates. When boiled with sodium carbonate, for example, the formation of sodium silicate is so considerable that soil thus treated acts strongly on solutions of potassium chloride, sulphate, or nitrate, exchanging sodium for potassium. The effect of boiling the soil with calcium chloride or sulphate is, however, much less marked. J. R.

Analytical Chemistry.

Substitute for Litmus. By G. Williams (*Chem. News*, **39**, 98).—The author advocates the substitution of ammonium dimethylamidoazobenzenesulphonate (the "orange" 3 of Porrier) for litmus in volumetric analysis. It is of an orange colour, and is turned pink by acids. It distinctly shows the presence of 1 part of sulphuric acid in 100,000 of water, whereas litmus ceases to indicate 1 part in 50,000. A great advantage it possesses over litmus is that it is not affected by carbonic acid or sulphuretted hydrogen. The best way to apply the test is, after each addition of acid from the burette, and the contents of the beaker having been well stirred, to allow one drop of the indicator to fall on the surface of the liquid. The indicator is thus distributed over a small space, and the reaction is more distinct. The results of the comparison of this indicator with litmus show the superiority of the former in a very satisfactory manner. L. T. O'S.

Bohr's Colorimetric Process for the Examination of Drinking-water. By Pusch (*Arch. Pharm.* [3], **14**, 227—239).—The apparatus necessary for the examination of drinking-water, together

with the reagents, in a portable form, are described. The colour is determined in the usual way by comparison with distilled water in a graduated 25 c.c. cylinder. The presence of iron is to be detected by the addition to 20 c.c. of the water of hydrochloric acid, potassium chlorate, and potassium ferrocyanide. Nitrites are determined by the addition of 5 drops of dilute sulphuric acid, 10 drops of zinc chloride, starch solution, and 5 drops of potassium iodide solution; as a control solution $2\frac{1}{4}$ mgrms. of potassium nitrite = 1·0 mgrm. of nitrous acid, are dissolved in 1 litre of water.

Detection of Ammonia.—Control solution: 1 cgrm. of ammonia solution of 0·96 sp. gr. = 1 mgrm. of ammonia per litre. Reagent: alkaline mercury potassium iodide solution. Of this 6—8 drops are to be added. If calcium, magnesium, or iron be present, these are to be separated previously by sodium carbonate.

Oxidisable Organic Matter.—Reagent: 0·01 normal oxalic acid solution = 63 cgrms. pure oxalic acid per litre; 0·01 normal permanganate solution = 35 cgrms. permanganate per litre. 50 c.c. of the water and 5 c.c. of dilute sulphuric acid are heated in a porcelain basin with 5 c.c. of permanganate; the excess of permanganate is determined by titration with oxalic acid.

Nitric Acid.—Control solution: 24 cgrms. of potassium nitrite = 14 mgrms. of nitric acid per litre. Reagent: brucine sulphuric acid solution 1 : 300. To 3 drops of the water, a like amount of the brucine solution is added, as well as a little pure concentrated sulphuric acid. The colour obtained is compared with that obtained by the addition of the brucine solution to the nitrite solution.

Chlorides.—Control solution: 33 cgrms. of sodium chloride = 2 cgrms. chlorine per litre. Reagent: Silver nitrate solution 1 : 20. Two cylinders are equally filled with pure water and that under examination, and to each are added 10 drops of silver nitrate and 5 of nitric acid. The cloudiness in the water should not exceed that of the distilled water.

Sulphates.—Control solution: 106 mgrms. of potassium sulphate = 5 cgrms. of sulphuric acid per litre. Reagent: barium chloride solution 1 : 10

Lime.—Control solution: 277 mgrms. calcium chloride in 1 litre. Reagent: ammonium oxalate solution 1 : 24. E. W. P.

Modification of Simpson's Method for Estimating Nitrogen By W. Hankó (*Deut. Chem. Ges. Ber.*, **12**, 451—453).—The apparatus consists essentially of a pear-shaped vessel provided with a stop-cock in the narrow neck. The other end is fitted with a perforated cork, through which two tubes pass; one of these communicates with an aspirator filled with solution of caustic soda, the other with the combustion-tube. By elevating the vessel containing the caustic soda and opening the stop-cock, the pear-shaped vessel is filled with the solution. Communication is then made with the combustion-tube, and the nitrogen is allowed to pass into the pear-shaped receiver. Over the top of this, above the stop-cock, there is a kind of pneumatic trough, in which the nitrogen can be collected in a suitable vessel when the combustion is finished. G. T. A.

Analysis of Organic Compounds containing Halogens or Nitrogen. By H. Schiff (*Liebig's Annalen*, **195**, 293—362).—The author's method is a modification of that described by Piria in his *Lezioni di Chimica Organica*, and consists of incinerating the substance in a platinum crucible inverted into a larger one. The substance is weighed off into the small crucible and intimately mixed with black flux, or a mixture of 1 part of sodium carbonate with 4 to 5 parts of lime; then the larger crucible is placed over it like a cover, and the whole inverted and exposed to the Bunsen flame. Piria himself used black flux mixed with saltpetre, and filled up the space around the edge of the inverted crucible with more or less of the same mixture. Liquids are enclosed in a little short-necked flattened bulb; the point is broken off as closely as possible to the bulb, which is then pressed down (with the point underneath) on a layer of soda-lime contained in the smaller crucible. For compounds containing iodine, sodium carbonate alone must be employed.

The author has also adopted a modified form of Piria's method of elementary analysis, which consists essentially in heating the substance in a small tray contained in a tube filled about three-quarters full of copper oxide, and through which a stream of oxygen is slowly drawn by an aspirator—almost the same method as that known as "Glaser's method." The author dispenses with the aspirator, and in many cases with the copper oxide. Piria recommends addition of copper filings to the substance in the tray when it contains nitrogen, in order to avoid evolution of nitric oxide. The author finds that in many cases no nitric oxide is formed if a part of the tube is raised to a red heat before the decomposition takes place, and the whole tube is kept at a red heat during the decomposition.

The length of copper oxide to be passed through appears to make no difference within very wide limits; 40 centimeters is amply sufficient. G. T. A.

The Moist Combustion Process: some Reactions of Alkaline Permanganate of Potassium. By J. A. Wanklyn and W. J. Cooper (*Phil. Mag.* [5], **7**, 138—140).—The authors have already shown that organic matter is burnt to carbonates, oxalates, and water, by heating with alkaline permanganate of potassium. In certain cases, however, acetate was produced, and this resisted further oxidation. They have now found that acetates are oxidised to potassium carbonate by heating to 160° or 180°, with considerable excess of alkaline permanganate and a little hydrated manganese dioxide. If the manganese dioxide be not added, oxygen is evolved. Even at a temperature a little over 100°, permanganate of potassium, when heated with caustic potash, evolves oxygen; at 140° the gas is very freely evolved in accordance with the equation $2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O$.

Chromic oxide yields potassium chromate when heated with alkaline permanganate solution; manganese dioxide is simultaneously produced. M. M. P. M.

Platinum-alloy Assay. By N. W. Perry (*Chem. News*, **39**, 89).—Charge the alloy (about 200 mgrams.) with silver sufficient to produce

perfect cupellation; about 150 mgrams. are generally required. Wrap the charge in sheet lead, and cupel until the lead is entirely gone. Weigh the button; loss = base metal. Flatten the button, anneal, roll out thin; anneal again, and make into cornet; part with concentrated sulphuric acid, boiling for several minutes. Wash, anneal, and weigh; loss from previous weighing = silver in original alloy + silver added for cupellation.

Alloy the cornet with at least 12 times as much silver as there is platinum present, form cornet as before, and part, first with nitric acid of sp. gr. 1·16, then with same acid of sp. gr. 1·26. Wash thoroughly, anneal in annealing cup, and weigh; loss = platinum. Treat residue with *aqua regia:* residue = osmiridium; loss = gold.

M. M. P. M.

Alum in Flour and Bread. By M. D. Penney (*Chem. News*, **39**, 80).—The author finds much larger quantities of alumina in flour than is generally supposed. Part of it is doubtless due to careless packing of the wheat used. The following tables give the results of his analyses. Egyptian wheat is largely contaminated with clay; this is said to be due to the manner of packing the wheat in the Nile boats:—

Table I.—*Six Samples of Flour.*

	Grains per 4 lbs.		
	Al_2O_3 as alum.	Fe_2O_3.	Siliceous matter.
1.	24·30	5·47	50
2.	21·75	6·06	55
3.	21·25	4·90	56
4.	17·00	5·20	40
5.	12·40	5·30	30
6.	6·34	4·77	22

Table II.

	Milligrams per 100 grams.		
Variety of wheat.	Phosphate of aluminium.	Phosphate of iron.	Siliceous matter.
1. Calcutta	24·30	18·10	164
2. Do.	21·00	15·16	184
3. Do.	18·50	20·00	170
4. Kourish	27·20	34·00	206
5. Do.	31·00	36·00	226
6. Russian	17·20	20·00	111
7. Do.	24·45	17·20	131
8. Do.	13·10	11·40	70
9. Do.	16·35	16·34	126
10. Chicago	4·00	9·00	48
11. Oregon	4·00	8·11	36
12. English	5·12	7·40	35
13. Do.	6·40	14·20	40
14. Do.	7·30	14·00	30
15. Do.	3·80	4·70	32

TALLE II (*continued*).

Variety of wheat.	Milligrams per 100 grams. Phosphate of aluminium.	Phosphate of iron.	Siliceous matter.
16. Stein	16·33	26·40	109
17. Do.	13·24	21·23	120
18. California	3·00	2·21	31
19. 11 varieties mixed	15·10	12·30	59
20. Egyptian as imported.....	167·00	64·50	370
21. Egyptian, hand picked.....	49·49	27·20	117
22. Egyptian, washed	14·10	6·36	101

The author is of opinion that there cannot be any more simple and certain qualitative test for the presence of alum in bread or flour than the logwood test properly applied. M. M. P. M.

Volumetric Estimation of Sugar. By F. W. PAVY (*Chem. News*, **39**, 77).—120 c.c. of Fehling's solution are mixed with 300 c.c. strong ammonia, and 580 c.c. water, and 20 c.c. of this blue liquid (= 0·01 gram sugar) are run into a flask fitted with a cork, through which pass the delivery tube of a burette and an exit tube, respectively. The burette is filled up with the saccharine liquid under examination; the contents of the flask are boiled, and the sugar solution is run in until the blue liquid is completely decolorised. The saccharine liquid should be somewhat dilute. The process depends on the fact that the cuprous oxide produced by the reducing action of the sugar is dissolved by the ammonia present as quickly as it is formed, and that if air be excluded the resultant liquid is colourless. The test solution also has the advantage over Fehling's solution of remaining unchanged when kept. M. M. P. M.

Estimation of Glucose in the Blood. By P. CAZENEUVE (*Compt. rend.*, **88**, 595—598).—The author criticises the process of Bernard (*Leçons sur la diabète et la glycogenèse animale*, *Cl. Bernard*, 1878). He considers (1) that the operations of the process are faulty; (2) that the reduction of the Fehling's solution is often uncertain towards the end of the reaction; and describes experiments to prove (3) that blood contains other compounds besides glucose which reduce the copper solution. The last observation has also been made by Musculus and Mering (*Compt. rend.*, Jan. 13th, 1879).

In addition to these objections, the author considers that the calculations of Bernard contain incorrect assumptions, and that therefore the figures given in the work above mentioned have only a relative value. J. M. H. M.

Specific Rotatory Power of Cane-sugar. By B. TOLLENS (*Dingl. polyt. J.*, **231**, 498—500).—In continuing his researches on the specific rotatory power of cane-sugar, the author obtains for

$\alpha_D\ 10 = 66{\cdot}475°$, a number which differs slightly from that formerly obtained according to the formula $\alpha_D\ 10 = 66{\cdot}8102 - (0{\cdot}015553 \times 10) - (0{\cdot}000052462 \times 10^2) = 66{\cdot}649°$, and also from that obtained by Schmitz $\alpha_D\ 10 = 64{\cdot}156 + (0{\cdot}051596 \times 90) - (0{\cdot}00028052 \times 90^2) = 66{\cdot}5274°$. As a mean $\alpha_D\ 10 = 56{\cdot}650°$ is obtained, which represents more accurately the specific rotatory power of cane-sugar in 10 per cent. solutions. In weaker solutions the specific rotatory power increases; in more concentrated solutions it diminishes. These numbers are calculated for cases in which the specific gravities are reduced to 4°, and in order to apply them at 17·5°—the usual temperature at which specific gravities are determined—the following formula is given:—$\alpha_D\ 10 = 66{\cdot}473°$, or nearly 66·5°, a number on which the tables calculated for sugar-polarisation are based. By adopting the formula for solutions in which $p = 20$—93, we obtain, according to $\alpha_D = 66{\cdot}355° + 0{\cdot}00724\,p - 0{\cdot}000196\,p^2$, for solutions containing approximately 26·048 grams sugar in 100 c.c., a specific rotatory power of 66·411°, and therefrom the correct weight 26·051 grams. According to Schmitz's formula we obtain for α_D of these solutions 66·322°, and a normal weight 26·086 grams. In all probability the mean of these, or 26·068 grams, should be taken. The Soleil-Dubosq apparatus requires 16·337 grams. For cases where the number of grams of sugar in 100 c.c. of a given solution is required, we may obtain according to the formula $p = \frac{\alpha \times 100}{\alpha_D \times 2}$, the number of grams in 100 c.c., corresponding with every angle, by introducing the number which corresponds with α_D. The latter is found by introducing at first an approximate number for α_D, say 66·5°, an approximation for p is thus obtained, and by the aid of the above formula the specific rotatory power for p is calculated, which number is then introduced into the formula, $p = \frac{\alpha \times 100}{\alpha_D \times 2}$, giving the more accurate number for p. D. B.

Estimation of Fatty Matters in Feeding-stuffs. By M. Siewert (*Landw. Versuchs.-Stat.*, **23**, 317—324).—For the extraction of fat from palm-nut cake and similar feeding-stuffs, the author recommends the use of carbon bisulphide instead of ether. He finds that ether is liable to contain impurities (sulphuric ethers) from which it cannot easily be freed, whilst carbon bisulphide may be readily purified by agitation with mercuric chloride and subsequent distillation. The disadvantages of using impure ether are, that it takes up substances other than fats, and that the residue left on evaporation cannot be dried so as to give a constant weight. Carbon bisulphide is free from these defects. The author finds that four hours' treatment with carbon bisulphide in a Tollen's apparatus is sufficient for the complete extraction of fatty matters for technical estimations. J. R.

Examination of Coffee, Tea, and Chicory. By C. Husson (*Ann. Chim. Phys.* [5], **21**, 419—426).—It is customary for the manufacturer to add to roasted chicory about 2 per cent. of butter or other fat in order to improve its appearance. To determine the nature of

this fat, and also to detect chicory when used as an adulterant of coffee, the author operates as follows. 10 grams of chicory are placed in a flask with 50 grams of glycerin and 20 drops of hydrochloric acid, and the mixture is brought to the boiling point. It is then filtered through linen, an equal volume of ether added, the whole well agitated, and the bottle placed in boiling water to promote the evaporation of the ether. As the latter evaporates, the dissolved fat collects on the surface of the glycerin, from which sufficient may be removed by means of a rod, and transferred to a microscopic slide. On allowing the slide to remain at rest for some time, the drops, at first oily, become eventually filled with crystals which are characteristic of the fatty matter employed. Stearic and margaric acids may thus be readily detected. Pure coffee, when treated in the same manner, does not give a similar crystallisation; the crystals consist of long fine needles, which present all the characteristics of ammonium or methylammonium chloride.

Caustic potash, fused in a test-tube with a little chicory, does not cause the evolution of ammoniacal vapours; but if coffee be substituted for chicory, methylamine is immediately disengaged, its vapour turning reddened litmus blue; the marcs of exhausted coffee, as might be expected, produce no crystals, neither do they disengage methylamine.

Tea, when treated in the manner already described, gives a crystallisation precisely resembling that obtained from coffee, and when fused with potash it evolves methylamine.

The remainder of the investigation is devoted to the microscopical character of powdered chicory and coffee, and plates are given representing the appearance of these substances when examined under moderate powers. — J. W.

Analysis of Caoutchouc. By D. Lindo (*Chem. News*, **39**, 99—101).—In the analyses of different samples of vulcanised caoutchouc, the percentage of ash varied from 62·7 to 32·07, that of zinc oxide from 60·71 to 15·3, and in three samples the percentage of calcium carbonate was 11·1, 30·29 (mean of three analyses), and 30·44 (mean of two).

The action of certain acids on the caoutchouc was attended with (1) the distension of the material; (2) appearance of small elevations on the surface; and (3) crimping of the edges. These effects are due to the absorption of acid by the material, the solvent action on the mineral matter, and in some cases on the caoutchouc, the softening of the material whereby the acid enters the pores more readily, and the small elevations are due to superficial distension.

Sulphuric acid, sp. gr. 1·828, decomposes the material in a few hours; when diluted with an equal volume of water, it dissolves out the zinc oxide pretty freely, except from those samples containing considerable quantities of calcium carbonate: it slightly impairs the elasticity, and does not produce crimping. When diluted with 19 times its volume of water, it dissolves appreciable quantities of zinc oxide.

Hydrochloric acid, sp. gr. 1·154, dissolves out considerable quanti-

ties of zinc, in some cases gas being evolved. After some time the caoutchouc assumes a red colour, and becomes decidedly crimped, and sulphur separates out. Heated with four times its volume of water it produces slight crimping.

Nitric acid, sp. gr. 1·374, decomposes caoutchouc rapidly; when the acid is diluted with 4 volumes of water, decomposition proceeds more slowly with slight crimping. When diluted with 9 volumes of water, the acid merely dissolves the metallic oxide, producing crimping.

Acetic Acid.—63 to 64 per cent. anhydrous acid has very little action on pure vulcanised india-rubber, but when it contains mineral matter, this is rapidly dissolved by the strong acid, the mass becoming distended and slightly crimped at the edges. The distension is greater when dilute acid is employed, for although it is produced more rapidly by the stronger acid, yet for this reason it is sooner arrested. The edges soon become crimped, which effect, if the acid is very dilute, is visible only on examination with a lens, by the aid of which it is possible to detect 1 part of anhydrous acid in 3,000 parts of water by the crimping of the edges.

It is possible that formic acid will exert a similar action.

L. T. O'S.

Detection of Ethyldiacetic Acid in Urine. By A. Hilger (*Liebig's Annalen*, **195**, 314—317).—The author detected this body in the urine of a diabetic patient by converting it into iodoform, and also by showing that it split up, with assimilation of water, into acetone, alcohol, and carbonic anhydride.

Repeated attempts to isolate the acid by adding acetic acid to the urine and shaking up with ether (Rupstein, *Centralb. f. Medicin. Wissenshaften*, 1874, 55) were unsuccessful.

Quantitative analyses depending on formation of iodoform were also made, which gave amounts of ethyldiacetic acid present in the urine of different days, varying in quantity from ·0399 to ·1909 in 100 parts.

Acetone and alcohol were also detected in the patient's breath condensed by passing it through a tube cooled with ice. G. T. A.

Technical Chemistry.

On the Preparation of Paper for Pigment or Carbon-photography. By A. Ott (*Dingl. polyt. J.*, **231**, 69—74).—For pigment paper various formulæ are given, for example:—

Nicholls.		Swan.	
Gelatin	100 parts	Gelatin	100 parts
Sugar syrup	50 „	Sugar.....	50 „
Water	250 „	Water ..	300 to 400 „

If these mixtures are to be made sensitive at once, a concentrated solution of 3 parts of ammonium dichromate is added—

	Bollmann.	Fargier.	Vidal.
Gelatin	100	100	100
Glycerin	33	—	13
Water	666	1000	666
Colouring material*	—	12·5	4

The author complains that in these recipes, which constitute the principal literature of the subject, the quality of the gelatin is not given, and that there are only two cases in which attention is given to the colouring material and chromic salts added. The other differences in the amounts of water, sugar, and glycerin used appear to him unsatisfactory.

Pigment papers may be prepared without either glycerin or sugar, if the gelatin be very soluble and the paper used at once, otherwise the paper dries rapidly, the gelatin becomes insoluble, and the picture cannot be developed.

The sugar and glycerin are employed to aid the hot water in penetrating the gelatin sheath; without it, the paper dries in two days after being rendered sensitive, and can no longer be developed, but the glycerin is only necessary in dry climates.

The author, relying on several years' experience, recommends the following formula:—

Gelatin	100 parts.
Sugar candy	25 „
Glycerin	5 „
Potassium dichromate dissolved in 50 parts of water	5 „
Water	300 to 400 parts.
Colouring matter	2 to 5 „

One of the most suitable kinds of paper is that of Romain Talbot. It is not a fine paper, but answers the purpose well, because the picture is transferred from it and the paper is slightly porous, so that in the development, it is penetrated by the water, and quickly peels off.

Gelatin.—He considers Nelson, Dale, and Co.'s. of London, the best, but thinks it expensive, whilst that of Arnette is not fit for use, having a bleaching effect on the colouring materials. Easily soluble kinds, such as Strasburg gelatin, are not fit for use unmixed.

For diapositive paper which must adhere directly to glass, Nelson's gelatin is exclusively employed.

Gelatin prepared from bones consists essentially of chondrin, and when mixed with chromium salts quickly loses its sensitiveness to light, as shown by Cooper.

Colouring Matters.—Carmine was formerly employed, but is now not used, owing to its being easily bleached by the light. The colouring materials employed must be of a certain specific gravity. If too heavy, they are apt to settle to the bottom. He recommends the following. Lamp-black (finest quality), sienna earth, umber, purpurin, alizarin, Prussian blue, all triturated to the finest condition.

* Sensitised with 13·3 parts of potassium dichromate.

The following is recommended as a formula for photographic papers with reddish tones:—

(*a*.) 6 grams lamp-black,
4 „ natural sienna earth,
12 „ burnt „
8 „ purpurin,
0·5 „ Prussian blue.

(*b*.) 5 grams lamp-black,
10 „ burnt sienna earth,
10 „ alizarin,
5 „ Prussian blue.

These quantities are reckoned to 1 kilogram of gelatin. To prepare the paper, it is passed between two rollers, the top one being of wood and the under one of metal. The latter dips into and revolves in a gutter containing the warm gelatin mixture, which it brings and applies to the paper in an even layer as it passes over the wooden roller.

The paper is then dried in a cool place in a current of air.

Preparation of the Mixture.—The gelatin is allowed to swell up in three quarters of the required quantity of water: the sugar dissolved in the remaining fourth, and the glycerin and colouring matter added to it, this mixture is then added to the gelatin, and the whole allowed to stand in a warm water-bath until the bubbles rise to the surface; it is then filtered through linen, and is ready for applying to the paper.

In spreading the gelatin, the temperature must be equalised, so that it is neither too thick nor too thin. On a band of paper 4 metres long, and 80 centimeters wide, about 300 grams of gelatin should be laid.

Arrangements are also given for producing photographs on paper tinted with two different colours: under these circumstances the two shades must not differ from each other too much.

For mountain and glacier views, paper with several differently coloured layers may be used with advantage in order to imitate the natural colours. W. T.

Calcium Chloride. By O. Gluge (*Chem. News*, **39**, 97).—In this paper, attention is called to the large quantity of calcium chloride obtained in the manufacture of bicarbonate of soda by the ammonia process, and which is generally thrown away. It is also suggested that endeavours should be made to ascertain if a more extended use could be made of this product which is produced at so low a cost.

L. T. O'S.

Macagno's Investigations on Bottle Glass. By H. E. Benrath (*Dingl. polyt. J.*, **231**, 145—152).—Macagno's investigations (*Chem. News*, **38**, 5) respecting the composition of bottle glass and its corrosion-degree, indicated by the solubility in water and the resisting power to a dilute solution of tartaric acid, seemed to show that our knowledge of the chemical composition of glass is no criterion for judging of its power of resistance, and that the degree of corrosion

cannot be determined by the amount of alkalis and lime present. The author has investigated this subject more minutely, and points out in the first place various erroneous statements which Macagno appears to have made in his paper; for instance, in valuing bottle glass, the numbers obtained from the analysis are added, and the sum divided by the number of analyses made in order to obtain the average composition of green, white, and other glasses. Green glasses may, however, contain as much as 20 per cent., and others scarcely 4 per cent. alkalis; one 56 per cent., the other 67 per cent. silicic acid; one may show the solubility in water = 1, the other 7·6. It is therefore wrong to regard the average composition of glass of the same colour as a criterion for judging of the quality of glass. The author thinks that it is not improbable that Macagno's statement that the red-brown and yellow-brown glasses are the worst, as regards the power of resistance, is founded on this mistake.

From the author's investigations the following conclusions may be drawn:—The resisting power of glass to water or acids increases in proportion to the silicic acid present. A certain relative amount of soda (alkali) exists which corresponds with the maximum of the resisting power, and which is to be found approaching the proportion of equivalent quantities of soda and lime. D. B.

A New Process for the Treatment of Iron and Copper Pyrites in the Dry Way. By L. Simonin (*Compt. rend.*, **88**, 586—587).—An account of experiments with Hollway's process, for obtaining copper matt from cupriferous iron pyrites in the Bessemer converter, as witnessed by the author at Sheffield. J. M. H. M.

Preparation of Malleable Nickel and Cobalt, and the Application of these Metals in the Pure State. By T. Fleitmann (*Deut. Chem. Ges. Ber.*, **12**, 454—455).—If magnesium in the proportion of one-eighth per cent. is added to nickel or cobalt, it becomes malleable and ductile, and susceptible of a high polish. The alloys do not alter in the air, and are well fitted for making harness, &c. They can also be welded to iron and steel at a white heat, and rolled into thin plates without separating from these metals. The same results could not be obtained with manganese, aluminium, calcium, &c. The addition of a minute quantity of magnesium to some other metals, *e.g.*, steel, causes a great alteration in structure. Whether the magnesium acts by destroying carbonic oxide, or from its great affinity for nitrogen by breaking up some compound, such as cyanogen, the author leaves undetermined. The *modus operandi* is to drop the magnesium through a hole in the cover of the crucible, having previously introduced a few pieces of charcoal to remove oxygen. G. T. A.

Coating Metals with their Oxides to guard them against Atmospheric Action. (*Dingl. polyt. J.*, **231**, 507).—By exposing iron to a very high temperature in a damp place, it becomes coated with a layer of ferrosoferric oxide. The latter possesses the property of resisting the action of the air and acid-vapours for a considerable time. A similar layer of oxide is produced with copper and lead.

Barff's method of preparing articles of iron which do not rust, is based on this circumstance. Brower, in St. Neot's, has improved this method; the principle, however, is the same. D. B.

Action of Sea Water on Iron and Steel Plates. By S. Kern (*Chem. News*, **39**, 35).—Plates of iron and steel, such as are used in shipbuilding, $\frac{1}{8}$-inch thick, were placed in sea water for 30 days; the iron plates lost about 26 grams; the steel about 22 grams in weight. M. M. P. M.

Use of Anthracite Dust in Du Puy's Process. (*Dingl. polyt. J.*, **231**, 506).—To reduce the iron ores in Du Puy's process of preparing wrought-iron direct from the ores, the valueless refuse from anthracite has been used with great success at the foundries of Reading, in Pennsylvania. The so-called "blue-billy" ores (residues from pyrites in the manufacture of sulphuric acid) have also been worked up according to Du Puy's method by Miller, Metcalf, and Parkin, in Pittsburgh, the results obtained being very satisfactory. The iron produced is said to compete with the best Swedish brands. Further trials on a larger scale are being made. D. B.

Iron Smelting in the Cupola Furnace. By F. Fischer (*Dingl. polyt. J.*, **231**, 38—42).—The process of combustion in the cupola furnace does not seem to be well understood. It has been calculated by E. F. Dürre from the quantity of coke consumed, the section of the blast pipe, and the wind-pressure, that 17 parts of carbon are burned to carbonic oxide and one part to carbonic anhydride, or 16·53 parts of carbonic oxide and 3·47 to carbonic anhydride, but that in Krigar and Eichhorn's cupola furnace the coal is completely burned to carbonic anhydride; 1,000 parts of iron require 100 parts of coke. The author quotes the calculation of A. Ledebur to show that 12 kilos. of coke are required to produce 100 kilos. of

Table I.

Time.		Carbonic acid.	Carbonic oxide.	Oxygen.	Nitrogen.	Remarks.
H.	M.					
3	15	7·2	2·4	10·8	79·6	At 3h. 20m. the blast begins.
3	28	16·9	5·1	0	78·0	Reddish-yellow flame appear.
3	40	14·8	—	0	—	1 c.m. of gas contained 76 cc.
3	56	14·9	7·9	0	77·2	Violet flame. [SO_2.
4	10	17·7	—	0	—	No flame.
4	15	16·0	5·6	0	78·4	Bluish flame.
4	30	15·3	7·2	0	77·5	
4	45	16·9	3·9	0	79·2	No flame.
5	4	14·4	8·6	0	77·0	Strong flame.
5	25	15·9	5·8	0	78·3	
5	40	18·3	0·4	0	81·3	
5	45	17·4	—	0	—	
6	0	18·0	1·2	0	80·8	Left off immediately after.

cast-iron, and his conclusion that the coke is completely burned to carbonic anhydride. The results of the author's analyses of the gases as carried out at iron foundries in Hanover are given in tabular form, of which the following is an example (p. 564).

On the day in which the above observations were made, the change consisted of :—

	Kilos.
Charging coke (Füllkokes)	360
Fusion coke (Schmelzkokes)	855
Iron	9,800
Lime stone	225
Total.....	11,240

From which were obtained :—

	Iron.
Iron	9,016
Slag	985
Total.....	10,001

The coke employed gave 6·98 per cent. of ash ; the slag had the following composition :—

Lime	16·03
Magnesia	0·48
Iron oxide	17·23
Alumina	6·01
Manganese oxide	2·98
Silicic acid	56·14
Sulphur	0·30
Alkalis and loss	0·83
	100·00

In the smelting of 1,000 kilos. of iron in these Krigar's furnaces, there is a loss of 80 kilos. Observations made at four iron foundries gave similar results on the whole as regards the composition of the gases, the loss of iron, and the composition of the slag. W. T.

Direct Process for Making Wrought Iron and Steel. By C. M. Du Puy (*Chem. News*, **38**, 35).—The process consists in heating ground iron ore, mixed with a flux and carbonaceous matter, in cases made of sheet iron, placed in a reverberatory furnace, squeezing the slag out of the molten masses, and rolling them into bars. The temperature employed is moderate and is not high enough to cause combination of phosphorus with iron ; almost every trace of the phosphorus is found in the slag. Lime is used as a flux ; it should be mixed in such a quantity as to ensure the formation of a glassy slag, which covers the semi-molten mass of iron, and thereby prevents oxidation. The cases in which the ore is placed may be about 16 in. diameter and 16 in. high ; they require neither tops nor bottoms. No mechanical working of the ore during the heating process is re-

required. Waste anthracite-dust answers admirably in place of more expensive forms of carbonaceous matter. The wrought iron and steel produced are of first-rate quality. M. M. P. M.

The Bessemer Process (Part II). By F. C. G. Müller (*Deut. Chem. Ges. Ber.*, **12**, 82—93).—The initial temperature of the German Bessemer process is about 14,00°, *i.e.*, the temperature of ignition of the carbon, but in the English process the initial temperature is 1200°, so that 0·8 per cent. of silicon must be burned before the combustion of the carbon begins. In the first stage of the German process a combustion of silicon and carbon take place; in the second stage the combustion of silicon ceases, but it is renewed in the last period. Lowering the temperature of the molten metal by the addition of cold iron increases the combustion of the silicon. This process has been investigated at several works in the north of Germany.

I. *Horch in Dortmund.*—The charge consisted of 7,500 kilos., two-thirds of which were Cumberland Bessemer iron, and one-third German Bessemer iron rich in manganese. After 4½ minutes 150 kilos. of rail ends were added:—

		Minutes.			
	Charge.	4½.	13.	16.	After addition of spiegel iron.
C....	3·52	2·78	0·428	0·053	0·228
βC ..	—	—	0·215	—	—
Si....	1·85	1·21	0·932	0·285	0·270
Mn ..	1·93	1·69	1·005	0·373	0·620

II. *Union Works in Dortmund.*—The charge of 8,000 kilos consisted of three-eighths English iron, three-eighths German, and two-eighths scrap steel. 3½ per cent. of rail ends were added after 10—13 minutes:—

		Minutes.		
	Charge.	5.	10.	After addition of spiegel.
C	—	—	—	0·332
βC....	—	—	0·280	—
Si....	2·03	1·136	0·830	0·166
Mn ..	0·686	0·412	0·296	0·817

III. *Osnabruck.*—The charge consisted of pure English Bessemer iron containing less than 0·5 per cent m.m.:—

		Minutes.		
	Charge.	5.	13.	18.
C....	3·74	3·074	0·852	0·107
Si ..	2·71	1·956 2·000	1·524	1·037

IV. *Bochum.*—The charge was composed of three-fifths German and two-fifths Cumberland iron, 8 per cent. of spiegel added:—

	Charge.	Minutes. 3¼.	6½.	9½.	11¼.	After addition of speigel.
C	3·96 3·78	2·97 2·99	1·751	0·299	0·075	0·418
βC ..	3·50	0·368	0·257	0·185	0·035	—
Si....	1·49	0·886	0·749	0·634	0·128	0·340
Mn ..	1·77	1·020 1·008	0·940	0·736	0·260	1·066

The following table shows (1) the composition of the metal immediately before the addition of spiegel; (2) after the addition; and (3) the composition of the spiegel:—

	1.	2.	3.
C	0·046	0·256	4·31
Si....	0·122 0·123	0·227 0·240	0·571
Mn ..	0·248	0·700 0·722	10·86

The absolute weight in kilos. of C, Si and Mn is shown below:—

	I. Before spiegel.	II. After spiegel.	III. Spiegel.	I+III.	I+III−II.	Oxygen required.
Total weight	7240	7800	600			
C	0·33	19·87	25·86	26·19	+ 6·32	+8·41
Si	8·83	18·17	3·63	12·46	− 5·71	−6·43
Mn.....	17·95	55·46	65·16	83·11	+27·65	+8·04

The presence of more than 3 per cent. of manganese in the Bessemer iron has a deleterious influence, since it increases the amount of silicon in the steel, $2SiO_2 + Mn + C = SiO_3Mn + Si + CO$. W. C. W.

Steel Welding. By S. Kern (*Chem. News*, **39**, 97).—Attention is called to the facility with which Russian Bessemer steel, containing about (?) 25 per cent. carbon, can be welded, and also to the fact that steel strips (6 in. × 4 in. × ¼ in.) after being welded could be beaten double through the weld at a dark heat without fracturing near or in the welded part, thus showing the good quality of the steel.

L. T. O'S.

Manganese Steel. By S. Kern (*Chem. News*, **39**, 118).—The use of steel containing more than 0·3 to 0·4 per cent. of manganese is to be avoided. That containing 1·5 to 2·0 per cent. of manganese, added for the purpose of neutralising the evil effects of phosphorus, being in most cases useless. L. T. O'S.

Preparation of Chrome-crucible Steel. By S. Kern (*Dingl. polyt. J.*, **231**, 505).—The author recommends the use of Bessemer or Siemens-Martin steel instead of puddle-steel for the preparation of chromium steel in crucibles, as by the ordinary method a product is obtained which varies in accordance with the quantities of carbon present

in the puddle-steel employed; moreover, the ferromanganese added generally yields phosphorus and sulphur in quantities which may injure the quality of the steel. In the author's process, the ferromanganese is replaced by chrome-iron ore and slaked lime.

D. B.

Utilisation of the Banana. By V. Marcano and A. Muntz (*Compt. rend.*, **88**, 156—158).—Flour made from the root of the banana tree was found to have the following percentage composition:—Starch, 66·1; fatty matters, 0·5; cellulose, 1·6; pectine, 1·4; cane-sugar, 0·6; inverted sugar, 0·4; nitrogenous matters, 2·9; tannin, organic acids, and non-nitrogenous extract, 9·4; mineral substances, 2·2; water, 14·9. This flour was grey and coarse; it could be kept without change. The proportion of nitrogenous substances contained in it being extremely small compared with the starchy matters, it cannot be used as an exclusive diet, but must be supplemented by animal food. The banana is, however, the chief support of the inhabitants of the equatorial regions; and in Venezuela the tree has spread so extensively that the wants of the population are supplied by a mere fraction of the fruit produced. In many places this fruit costs nothing beyond the expense of gathering, and it has become a question whether it cannot be made to yield some products for exportation. The flour yields tolerably pure starch; and the fruit which arrives in Paris ripe and in good condition, undergoes alcoholic fermentation when left to itself, yielding by one distillation a spirit of 52 degrees centesimal, having a pleasant smell and taste. An analysis of the pulp of a variety of banana very common in Venezuela gave the following results:—Cane-sugar, 8·5; inverted sugar, 6·4; starch, 3·3; fatty matters, 0·3; cellulose, 0·2; pectin, 0·6; nitrogenous matters, 1·6; mineral matters, 1·1; water, 73·8; extract, &c., 4·2. The pulp constituted six-tenths of the fruit; the husk which formed the remainder contained also 1·6 per cent. of inverted sugar. R. R.

Ghea- or Shea-butter. By C. Deite (*Dingl. polyt. J.*, **231**, 168—171).—This fat is prepared from the seeds of *Bassia*, a tree growing in India and the western parts of Africa. Various species of the order bassia yield fat, that from which ghea-butter is obtained being called by Kotschy *Butyrosperum Parkii*; by Olivier, *Bassia Parkii*. The fruit from which this fat is extracted is the size of a pigeon's egg. A thin husk surrounds a fleshy substance possessing an agreeable taste. This substance covers a kernel from which the butter is prepared in the following manner. The kernels are dried in the sun, pounded, placed in large earthenware vessels, and boiled with water. The fat which rises to the surface is skimmed off. It is of a grey- or green-white colour, and has a peculiar tough, sticky consistency, similar to a mixture of fat and turpentine, and possesses a peculiar aromatic smell. It may be kept for a considerable time without turning rancid, and is therefore used very largely as lard. According to Thomson and Wood its melting point is 43·3°; Château gives 29°, and the Brussels Stearin Company 23° to 24°. Thomson and Wood have obtained a solid acid from this fat, melting at 61°, which they call margaric acid. According to Oudemanns, this substance is a mixture of a solid fatty acid,

melting at 61°, and a liquid acid. The former is stearic acid, and, according to Pelouze and Boudet, the liquid fat is oleïn. By treating ghea-butter with concentrated sulphuric acid and distilling, fatty acids melting at 52—54° are obtained, which, when pressed, give a stearin melting above 60°. In spite of its high melting point, this substance is soft and friable—a circumstance which is due to the fact that it is pure stearic acid and not a mixture of solid fatty acids. It is therefore necessary to mix this fat with palmitin or some other solid fat, otherwise it is difficult to use it in candle making. On the coast of Coromandel this fat is used for soap-making, the product obtained representing a hard, white mass, which, however, does not form a lather. D. B.

The Time of First Racking-off New Wines. By C. Weigelt (*Landw. Versuchs-Stat.*, **23**, 325—334).—A technical paper, referring especially to the wines of Alsace.

Dochnahl's New Method of Preparing Wine. By C. Weigelt (*Dingl. polyt. J.*, **231**, 489—495).—The author undertook a series of trials with a view of determining whether the above method gives a wine possessing the chemical and physiological properties of a good quality wine. According to Dochnahl, 1,000 litres must, as a rule, produce when pressed about 800 litres of wine, whereas, without pressure, about three-fourths of the liquid must may be decanted. By treating the residue with 480 litres of water and 342 lbs. of grape-sugar a further quantity of 600 litres may be decanted. By repeating this treatment twice, a second and third product of 600 litres in each case is obtained. By this method, therefore, 1,800 litres of wine are obtained, besides that yielded by the original must, all of which is said to be of first-rate quality as regards flavour and bouquet. From the lees, an additional amount of a second quality wine may also be obtained. The author has prepared wines according to this process. He found, however, that it was impossible to obtain the above-mentioned yields. Chemical analysis of the products clearly showed that they had been prepared by the aid of artificial grape-sugar. The wines, moreover, were deficient in flavour and bouquet. D. B.

The Malt-Test. By W. Schultze (*Dingl. polyt. J.*, **231**, 53—56).—W. Schultze has, under the above title, undertaken a revision of our theoretical views on the mash-process, and gives some important practical hints.

First of all, he inquires whether the usual mash temperature of 70° to 75° in the malt-test is the right one. To determine this, he took 100 grams of dry malt and mashed it at different temperatures until the starch reaction disappeared, and then determined the amount of extract according to the corrected proportional method, and on the basis of the new extract-table.

Five kinds of malt were taken and submitted to the process at five different temperatures from 72·5° to 60°. From the results, it appeared that the smallest amount of extract was always obtained at temperatures between 70° and 75°. It was also found that the time occupied

by the process bore a constant relation to the amount of extract obtained: the lower the temperature, down to 60°, under which the process was carried on, the larger the amount of extract obtained, but the longer the time required.

Kind of malt.	At 70°.	At 65°.	At 63°.	At 60°.
	Min.	Hours.		
A	20	5½	11½	18½
B	15	4½	10¾	18
C	15	4	10	17½
D	10	2½	5½	11
E	10	3	6	—

From this table it is seen that a rapid transformation of the starch into extract takes place in mashing at 70° only. A higher temperature is not only unnecessary but injurious, because some kinds of malt mashed at 72·5° produce an opalescent wort. The malt-test should therefore be conducted with a mash-temperature of 70°, and the process should occupy from ten to twenty minutes. A longer time is proved to be superfluous.

Different kinds of malt mashed until the disappearance of the starch reaction, gave results of which the following is an example:—

Kind of malt. I.	18½ hours at 60°.	11½ hours at 63°.	5½ hours at 65°.	Alternate ½ hours at 65° & 70°.	20 min. at 72·5°.
Extract	80·09	79·24	78·53	77·82	76·13
Maltose	61·93	57·45	52·99	48·55	44·04
In 100 parts of extract there are of maltose	77·32	72·50	67·48	62·39	57·85

From this table it is again seen how important time is as a factor in the mash-process. In practice, it is not possible to carry on the process for ten hours. It is scarcely practical for six hours to keep the temperature at 63°. On the other hand, at 70° and upwards, there is a smaller amount proportionably of maltose formed, and starch remains in the malt-dust. Dr. Griessmayer has endeavoured to avoid this drawback by a process patented some time since. He seeks to obtain a greater amount of extract and maltose by employing a temperature of 65°, and to preserve the character of Bavarian beer by boiling the mash. W. T.

Tenacity of Starch. By G. Whewell (*Chem. News*, **39**, 97).—To test the tenacity of potato starch used for the sizing and stiffening of yarn and cloth, the author employs a modification of Shier's

method. The principle consists in ascertaining the number of grains weight of starch, which, after being made into a jelly, will support a 100-grain weight for five minutes, without breaking the skin. To determine the tenacity of a sample of starch, 6 conical test-glasses, 1 oz. capacity, were labelled 18, 20, 22, 24, 26, and 28; 18 grains of the starch are mixed with 26 c.c. water, boiled for three minutes, and poured into the test-glass marked 18, and so on for the other test-glasses, using the number of grains of starch corresponding to the number on the glass. After cooling for two hours a 100-grain weight ($\frac{13}{20}$ inch in diameter) is placed on the jelly for five minutes; if it is supported for more than that time, it is placed on each of the others until one is found through which it sinks; this gives the tenacity within 2 grains, the number of grains required being the tenacity; that is to say, if the tenacities of two samples are 18 and 28 respectively, it means that 28 lbs. of one sample will give the same stiffness as 18 lbs. of the other. On p. 122 (*Chem. News*, **39**), Mr. W. Thomson points out that this method may give fallacious results, to which the author replies on p. 134. L. T. O'S.

New Fast Green, or Malachite Green. By Bindschedler and Busch (*Chem. News*, **39**, 61).—A green pigment may be prepared directly from dimethylaniline by the action of benzaldehyde and zinc chloride on the latter body (*Ber.*, **10**, 1623), or by substituting trichlorobenzene for benzaldehyde. Working details are not given. Methyl greens can be distinguished from these greens produced by direct processes, by the fact that wool, silk, or cotton dyed with methyl greens turns violet when heated to 120°, but is not changed at that temperature when dyed with direct greens. M. M. P. M.

Colouring Matters. (*Dingl. polyt. J.*, **231**, 173—177).—*Benzene.*—According to Marzell, 100 litres of commercial "benzole," boiling between 80—150°, give the following fractions:—

	Litres.	Boiling point.
Benzene and lower boiling portions	6	62 to 80°
Benzene.....	44	80 „ 82
Mixture of benzene and toluene.....	6	82 „ 110
Toluene.....	17	110 „ 112
Mixture of toluene and xylene	5	112 „ 137
Xylene	9	137 „ 140
Mixture of xylene and higher boiling portions.....	5	140 „ 148
Residue.....	8	148 „ 150

According to Salzmann and Wichelhaus benzene may be obtained by passing vapours of lignite tar over platinised asbestos or animal charcoal. This reaction can only be explained by a splitting up of the hydrocarbons, whereby the gas evolved makes up the product richer in hydrogen.

Preparation of Blue Colouring Matters from Dimethylaniline.—To a cold solution containing 10 kilos. dimethylaniline, 30 kilos. concen-

trated hydrochloric acid, and 200 litres water, a solution of 5·7 kilos. pure sodium nitrite in 200 litres water is added slowly, with constant agitation. To reduce the nitroso-dimethylaniline hydrochloride formed to amido-dimethylaniline, the mixture is brought into closed wooden vessels, fitted with agitators, and provided with pipes for carrying off the excess of hydrogen sulphide. It is treated with 500 litres of water and 50 kilos. concentrated hydrochloric acid. Hydrogen sulphide is then introduced until the yellow colour disappears. The mixture is in the next place treated with 200 litres of a solution of ferric chloride of 1·07 sp. gr., then saturated with sodium chloride, and treated with zinc chloride, until all the colouring matter is completely precipitated. After filtration, the blue colouring matter is extracted with water from the precipitate. The solution is again saturated with sodium chloride, precipitated with zinc chloride, filtered, the residue pressed, dried, and brought into commerce in this form.

According to Meldola, when diphenylamine is dissolved in glacial acetic acid and nitrous acid introduced into the solution, a yellow crystalline mass separates, which is collected and washed with water. By boiling with alcoholic soda-lye, it gives a deep red liquid, which separates a yellow colouring matter, when diluted with water. This substance dyes silk and wool with a fine yellow colour. Its composition is at present unknown. D. B.

Chrome Black on Wool. By M. Reimann (*Deut. Chem. Ges. Ber.*, **12**, 180—182). The cheapest black for wool is obtained by boiling the wool in a mixture either of dilute sulphuric acid and potassium dichromate, or of sulphuric acid, potassium dichromate, potassium bitartrate, and copper sulphate, and subsequently dyeing with logwood. The author now proposes to use instead of these, a mixture of chrome-alum, iron-alum, and bitartrate with logwood. For the chrome-alum, the impure solutions of it obtained as bye-products in many manufactures may be substituted. The iron-alum in this process not only serves as an oxidising agent, taking the place of chromic acid and copper sulphate in the first two mixtures, but also deepens the black by itself, forming a compound with the logwood. The advantages claimed for the process are :—1st, since no chromic acid is contained in the mixture, the wool is not oxidised, and does not become hard to the touch; 2nd, the black is a mixture of chrome and iron-black, and, whilst having the good qualities of both, is free from the drawbacks of either. Chrome-black is unaffected by acids, but is injured by alkali and by exposure to light; whilst the iron-black has exactly opposite properties. Ch. B.

General and Physical Chemistry.

Illumination of the Lines of Molecular Pressure, and the Trajectory of Molecules. By W. Crookes (*Compt. rend.*, 88, 174—176).—The author has found that the size of the dark space which surrounds the negative pole in a Geissler's tube varies according to the perfection of the vacuum, the nature of the gas, the temperature of the negative pole, and, in a less degree, according to the intensity of the spark. When a radiometer having vanes made of aluminium covered on one side with mica, was placed in a partial vacuum, a violet light spread over the metallic surfaces, but when the vane was made the negative pole of an induction coil, the mica remained dark. When the pressure of the gas was diminished, a dark space was seen to divide the violet light from the metallic surfaces; and when it had been reduced to 0·5 mm. the dark spaces extended to the glass, and rotation commenced. Further improvement of the vacuum caused the dark spaces to increase, and apparently to flatten themselves against the glass, and the rotation then became extremely rapid. When the arms of the radiometer carried hemispherical cups instead of vanes, the dark spaces took the shape of the cups, and rotation began when the dark spaces on the concave sides reached the glass. The dark space presented by a concave surface was studied in a fixed negative pole of that form. It was observed to have the shape of an irregular ellipsoid, inflected towards a luminous point, which may be termed the focus, as the appearance presented was strikingly similar to that produced when a concave mirror reflects the solar rays in a foggy atmosphere.

With respect to the above, T. du Moncel remarks that the dark space may be distinctly observed under the ordinary pressure, when the induction spark is taken between two glass plates, and is examined by the microscope. The negative electrode will then be seen to be covered with a beautiful blue-violet light, the dark space seeming to shape itself on the contour of the negative pole. R. R.

Radiation from Incandescent Platinum. By J. Violle (*Compt. rend.*, 88, 171—173).—The author made a certain number of determinations of the intensity of the red light emitted by platinum at temperatures between 900° and 1775°, its fusing point. He gives an empirical formula representing these results, the intensity I of the light at the temperature t being—

$$\log. I = - 8{\cdot}244929 + 0{\cdot}011475\,t - 0{\cdot}000002969\,t^2.$$

From this formula he deduces certain theoretical consequences, such as that the intensity of the *red* light would attain a maximum at a temperature of 1933°, &c. He suggests that the temperature of a furnace might be ascertained by the easily made photometrical determination of the intensity of light given off by a piece of platinum placed in it.

On transmitting the radiation from fused platinum through rock-salt and alum respectively, he found that the luminous heat passing through the alum was $\frac{2}{9}$ of the total heat passing through the rock salt, and, as Dessains has found in the spectrum of incandescent platinum only an insignificant fraction of luminous heat (*ibid.*, **84**, 285), the author concludes that at 1775° the more refrangible radiations have a higher relative value in the spectrum of platinum than at a point a few hundred degrees lower. R. R.

New Universal Stand for Use with the Pocket Spectroscope. By F. v. Lepel (*Deut. Chem. Ges. Ber.*, **12**, 263—266).

Displacement of the Lines of the Spectrum by the motion due to the Sun's Rotation. By L. Thollon (*Compt. rend.*, **88**, 169—171).—The paper describes the arrangement of apparatus by which the author was enabled to view the spectra, one above the other, of two portions of the margin of the sun's disc, situated at the opposite extremities of his equatorial diameter. The spectroscope made use of had a dispersive power equal to about 30 prisms. The lines of the one spectrum did not appear as prolongations of the lines of the other spectrum, but a marked displacement was evident, which was greatest in the more refrangible part. The telluric lines did not undergo any such deviation, and one of them, very near to the nickel line between D_1 and D_2, rendered the displacement of the nickel line very conspicuous. The amount of the displacement appeared to agree with the results of calculations based on the undulatory theory, but the author hopes to obtain more decisive results by a better disposition of his apparatus. R. R.

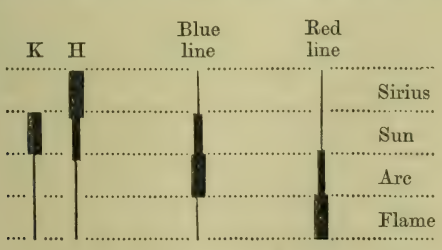
A Cause for the Appearance of Bright Lines in the Solar Spectrum. By R. Meldola (*Phil. Mag.* [5], **6**, 50—61).—The existence of bright lines of oxygen and nitrogen in the solar spectrum, which was pointed out by Draper, is explained by the assumption that in the outer portion of the sun's atmosphere the temperature is low enough to permit of chemical combination. The molecular weight of oxygen (and nitrogen) being small, these substances would extend to a great height in the solar atmosphere, and would reach the cooler zone, where the oxygen would combine with the hydrogen also present, producing vivid incandescence; other substances of low vapour-density might also take part in the combinations going on; the heavier vapours, however, not reaching to the cool zone, would not be represented by bright lines. This hypothesis is rendered probable by considerations such as the following. Since metals of great vapour-density (Fe, Ni, &c.) are frequently thrown up into the chromosphere, oxygen must extend to regions far beyond, and therefore far cooler; now the band spectra observed in the nuclei of sun-spots would seem to indicate that the temperature in these regions is low enough to admit of the formation of compounds, *à fortiori*, such combination would be possible in the zone exterior to the chromosphere.

The fact that whilst the oxygen lines appear bright, the hydrogen lines are very dark, is explained if we remember that the lines of the

metals are much more intense than those of non-metals; since the absorptive power of metallic vapour is proportionally great, the bright rays of hydrogen emitted by the photosphere would be entirely absorbed in the reversing layer, forming intense dark lines; the oxygen rays would, on the other hand, yield dark lines of very moderate intensity: as the light passed through the outer incandescent region, the dark lines of hydrogen would be rendered less intense, but would still remain as distinct dark lines, whilst the dark oxygen lines would be obliterated, and moderately bright lines substituted for them.

The hypothesis of a zone of combustion in the higher regions of the sun's atmosphere may further explain the brilliancy of the helium line (D_3), by supposing that the light which furnishes this line is emitted by this zone; it also opens the question as to whether the so-called "telluric" lines may not be due to the presence of aqueous vapour in the outer portions of the sun's atmosphere. F. D. B.

Researches on Spectra. By J. N. Lockyer (*Compt. rend.*, **88**, 148—154).—The author attributes to successive dissociations the changes which are observed in spectra yielded by the same so-called element at different temperatures. He conceives that many of those substances which our laboratory experiments have hitherto failed to resolve into anything simpler, and which are therefore reputed to be elements, are nevertheless complex in reality, and are capable of becoming dissociated into true elements by a temperature sufficiently high. A gradually increasing temperature would in such cases occasion progressive dissociation of the various elements in succession, and the spectrum lines due to each real element would appear in their maximum intensity when the heat had reached that point at which that constituent became completely dissociated from the rest, and before the heat had become sufficiently great, or had acted for a time sufficiently long to eliminate it altogether. This accounts for the changes and inversions of the relative intensities of the lines according to the temperature. These views are explained in the original paper by diagrams and representations of parts of the different spectra of calcium, &c., as produced artificially in various ways, and as observed in the sun, and in Sirius, which star, the author remarks, is hotter than our sun. One of these diagrams represents calcium spectra nearly as below:—



The most important general principle enunciated in the paper is, that the several lines of the spectra of the so-called elements cannot result from the vibrations of similar molecules. The author says that

he first propounded this idea in 1874, and that he has more recently shown that the molecular grouping of the calcium atoms is resolved by very elevated temperatures into other groups of atoms, which have their principal lines in the violet part of the spectrum.

In support of the view by which the substances now called elements are to be regarded as compounds, the coincidence is adduced of certain lines belonging to different elements. The coincidence of the *h* line of hydrogen with one of the indium lines suggested to the author an experiment in which a loose fragment of indium was placed within a Geissler's tube, and could be made to serve as an electrode when required. When the spark was taken from the indium, the red and blue lines of hydrogen were seen with a notable increase of brilliancy. To obviate the objection that this might be due to occluded hydrogen, the author repeated his experiment with electrodes of palladium charged with hydrogen, without being able to obtain the spectrum of that gas. The hydrogen in the indium was not therefore in the state of occluded gas. R. R.

Thermic and Galvanometric Laws of the Electric Spark. By E. Villari (*Compt. rend.*, **88**, 706—709).—The thermic effect produced by the spark in the discharge of a battery of Leyden jars, is proportional to the quantity of electricity which passes, and to the length of the spark. R. R.

Treatment of Bunsen's Cells. By F. Beilstein and L. Jawein (*Deut. Chem. Ges. Ber.*, **12**, 448).—The authors recommend the covering of the bright metallic parts in these cells with oleonaphtha, an oil prepared from Caucasian petroleum. This prevents the rusting of these parts, and the consequent resistance to the current. P. P. B.

Pressures produced by Galvanic Deposits. By Bouty (*Compt. rend.*, **88**, 714—716).—The paper relates to the fact observed by Mills (*Proc. Roy. Soc.*, **26**, 504) of the contraction of the bulb of a thermometer when coated electrolytically with a deposit of metal. Mills has stated that the deposit of zinc and that of cadmium are exceptional in causing a dilatation of the bulb instead of a contraction; but the author finds that deposits of these metals act like the rest in exercising a pressure. A theoretical formula given in the paper expresses the pressure on a cylindrical reservoir in terms of its compressibility, radius, &c., and of the coefficient of compressibility of the deposited metal. This coefficient, as determined from the contractions observed in a series of experiments, has for copper the value ·000001235, while Regnault found directly for red copper ·000001317. The theoretical maximum pressure for an absolutely resisting cylinder would be about 350 atmospheres for a deposit of copper: the greatest pressure actually observed was about 100 atmospheres. A bulb of a very flattened elliptical section would be subjected to pressures increasing so rapidly at the extremities of the major axis, that its shape would tend to become circular, and the mercury would sink in the stem. R. R.

Magnetic Rotatory Power of Gases at ordinary Temperature and Pressure. By H. Becquerel (*Compt. rend.*, **88**, 709—712).—

The apparatus employed for the experiments described in this paper consisted of a copper tube, 3 meters long and 12 cm. in diameter, having its end closed by glass plates with parallel faces. The tube was mounted horizontally and surrounded by a very large coil, composed of six sections, each containing 15 kilos. of copper wire 3 mm. in diameter. The current from a battery of 66 nitric acid cells circulated through the coil to render the interior of the tube a magnetic field. A lime light was the source of light, and by means of plane mirrors of silvered glass the rays were reflected and made to traverse the tube nine times successively, making the effect equivalent to a passage through a gaseous atmosphere 27 meters in length. Reversal of the direction of the current permitted the double rotation of a polarised ray to be measured. Coal-gas at ordinary temperature and pressure gave to polarised yellow light a double rotation of + 6·8 for the 27 metres traversed. This rotatory power accords nearly with that deduced from a theoretical formula, $n_2\ (n_2-1)$, in which n is the index of refraction. With the vapour of carbon bisulphide, as well as with coal-gas, the author was able to verify the fact of the unequal rotation of the planes of polarisation of rays of different colours.

Oxygen gas, like other strongly magnetic substances, exhibited a negative rotatory power; but at ordinary temperatures and pressures the amount was too small to admit of accurate estimation. The author has before shown (*Compt. rend.*, **85**, 1227) that the negative rotations do not vary for rays of different wave-lengths in the same way as the positive do. R. R.

Magnetic Rotatory Power of Vapours. By E. Bichat (*Compt. rend.*, **88**, 712).—The apparatus used in the author's researches comprised two concentric brass tubes, 3·6 meters long. The inner tube was closed at the end by plates of glass, and in the annular space between the tubes a current of hot water, hot oil, or steam, was made to circulate. The electric current was furnished by a battery of 80 large Bunsen cells. The rotation of the plane of polarisation produced by the same current was observed from zero to the boiling point of carbon bisulphide, and that of tin chloride, $SnCl_4$. The results showed that the molecular rotatory power was maintained until the temperature rose nearly to the boiling boint of the liquid. After this a diminution occurs, much more rapid than could be foreseen from considerations based on the relations of the densities. The author hopes, however, to be able ultimately to improve the methods employed, so as to ascertain if there is an invariable relation between the magnetic rotatory power of a liquid and that of its vapour. R. R.

Electrolysis of Water. By F. Exner (*Ann. Phys. Chem.* [2], **6**, 336—353), **and Galvanic Polarisation.** By F. Exner (*Ann. Phys. Chem.* [2], **6**, 353—384).—The object of the experiments recorded in the first of these papers is to prove that the electrolytic decomposition of water takes place whenever the electromotive force of the primary current exceeds in the smallest degree the electromotive force of the simultaneously developed polarisation. In his experiments the author

used electrodes of the finest platinum wire, and these were viewed through a lens, in order that the first indications of the extrication of gas might be observed. The primary current was derived from a thermopile, so arranged that the electromotive force could be gradually increased by bringing more and more elements into the circuit. The electromotive forces of the primary and polarisation currents were measured by methods described in *Ann. Phys. Chem.*, **6**, 338. Up to about 2·00 Daniell cells, the primary current developed a polarisation electromotive force equal to its own. When the primary current was equal to 2·30 Daniell, the polarisation current was equivalent to 2·03 Daniell, and at this value it remained constant, notwithstanding the further increase of the primary current. The decomposition was first observed at this point, namely, when the primary current had an electromotive force exceeding that of the polarisation current by 0·27 Daniell. These were the results with pure water free from dissolved gases; the effects of adding a few drops of sulphuric acid were that the decomposition commenced with a somewhat weaker primary current, and the excess of its electromotive force over that of polarisation was now only 0·09 Daniell. With electrodes of copper immersed in dilute sulphuric acid decomposition first took place with a primary equal to only 0·54 Daniell, and exceeding the polarisation current by only 0·03 Daniell. Similar experiments with other metals led to the conclusion that an effective electromotive force of less than 0·03 Daniell suffices to decompose water. A general law of electrolysis is derived from the discussion of these experiments, namely, that in any closed circuit, of which an electrolyte forms a part, the electrolyte is decomposed as soon as an effective electromotive force, however small, predominates throughout the general circuit.

The researches described in the second paper have for their object to prove that there is no essential difference between a polarisation element and an ordinary one. The source of the current is, in the latter, the oxidation of zinc; in the former it is the oxidation of hydrogen. The paper gives in detail the numerical results of experiments with different substances, the experiments forming 29 series. The correctness of the author's conclusion is exemplified by a table showing the close correspondence of the calculated and the observed electromotive forces of polarisation currents in 24 cases where different electrolytes and electrodes were employed. The discussion of the results includes some observations on the theories of electrolysis and related subjects. R. R.

Galvanic Polarisation of Platinum in Water. By F. Exner (*Ann. Phys. Chem.* [2], **5**, 388—405).—The different values which observers have found for the maximum polarisation of platinum in the electrolysis of water, led the author to investigate the circumstances which may have caused these differences, and to inquire in what way the electromotive force of the polarisation current increases when that of the primary current increases from 0 to a point beyond the maximum of the polarisation.

A quadrant electrometer was used to measure the electromotive force both of the battery and of the voltameter, that of the battery

being first found. The battery was connected with the voltameter for a time, and then by means of a switch, the battery was instantaneously thrown out, and the electrodes connected with the quadrants of the electrometer. Two circumstances were found to have very great influence, firstly, electrolytic conduction, in which the hydrogen set free recombines with the oxygen already dissolved in the water. This only causes a redistribution of the oxygen as far as it occurs, and the polarisation of the electrodes is always less than that of the primary current. The extent to which it takes place depends on the shape of the electrodes, and is least when they have the least surface, as the gas is then evolved too quickly to combine with the oxygen. It may be almost entirely obviated by employing fine platinum wires. It also disappears when the water is free from gas. In this case the electromotive force of the polarisation is always equal to that of the primary current up to its maximum, which, however, varies with the second modifying circumstance, the formation of hydrogen peroxide by a secondary action. The conditions of the experiment have a very great influence on this, for instance, the higher the temperature the less the amount formed, and the lower the maximum polarisation.

J. H. P.

Vapour-Density of Aqueous Acids with constant Boiling Points. By A. Calm (*Deut. Chem. Ges. Ber.*, 613—614).—A determination of the vapour-densities of aqueous formic (b. p. 105°), hydrobromic (b. p. 126°), and hydrochloric (b. p. 110°) acids, shows that these substances are mixtures and not definite hydrates.

W. C. W.

Vapour-Densities of some Inorganic Bodies. By C. and V. Meyer (*Deut. Chem. Ges. Ber.*, **12**, 609—613).—The vapour-density of phosphorus pentasulphide (m. p. 274—276°), prepared by heating a mixture of amorphous phosphorus and sulphur, and purified by distillation, was found to be 7·67. This shows that dissociation does not take place.

The density of indium chloride vapour, viz., 7·87, shows that the molecular formula of this substance is $InCl_3$, and not In_2Cl_6.

W. C. W.

Nature of Cohesion and its Chemical Signification. By F. Mohr (*Liebig's Annalen*, **196**, 183—213).

Specific Gravity and Atomic Volume of the Cerium Metals. By R. Hermann (*J. pr. Chem.* [2], **19**, 172—173).—The following table contains the author's results. By comparing the group of earth-metals with the cerium group it is evident that the latter metals form a peculiar group standing midway between the earth-metals and the metals of the iron group:—

I. *Earth-Metals and their Oxides.*

Formula.	Atomic weight.	Atomic vol.	Sp. gr. Calculated.	Sp. gr. Observed.
$\frac{Be}{1}$	9·2	5·0	1·84	1·93
$\frac{Zr}{1}$	44·8	10·5	4·26	4·15
$\frac{Y}{1}$	61·6	16·0	3·85	3·77
$\frac{Er}{1}$	112·6	16·0	7·08	?
$\frac{Th}{1}$	119·0	16·0	7·43	7·65
$\frac{BeO}{0{\cdot}66\ 1}$	25·2	8·33	3·02	3·02
$\frac{ZrO}{0{\cdot}66\ 1}$	60·8	12·0	5·06	4·90
$\frac{YO}{0{\cdot}66\ 1}$	77·6	15·66	4·96	4·84
$\frac{ThO}{0{\cdot}66\ 1}$	138·0	15·66	8·71	9·13
	II. *Cerium-Metals.*			
$\frac{Ce}{1}$	92·0	13·50	6·81	6·728
$\frac{Di}{1}$	95·0	14·50	6·55	6·54
$\frac{Ln}{1}$	92·6	15·50	5·97	6·07
$\frac{CeO}{0{\cdot}75\ 1}$	108·0	15·12	7·07	?
$\frac{DiO}{0{\cdot}75\ 1}$	111·0	15·87	6·99	6·85
$\frac{LaO}{0{\cdot}75\ 1}$	108·6	16·72	6·39	6·53
$\frac{CeO + CO_2}{0{\cdot}75\ 1\quad 1\ 1}$	232·0	38·62	6·00	6·00
$\frac{CeO + 2\left(\frac{CeO_2}{1\ 1}\right)}{0{\cdot}75\ 1}$	356·0	62·92	5·73	5·77

M. M. P. M.

Chemical Affinity. By GULDBERG and WAAGE (*J. pr. Chem.*, [2], **19**, 69—114).—In the year 1867 the authors published a memoir, "Études sur les affinités chimiques," in which they discussed the influence

exerted by the mass of the reacting substances on a series of chemical changes. They there showed that the result of a chemical process is dependent, not only on the mass of those bodies which directly take part in the formation of the products of the change, but also on the mass of those substances which are not themselves chemically changed. They distinguished between the true forces of chemical affinity and the secondary forces whose action is to be traced to the presence of foreign bodies, *i.e.*, bodies which do not directly participate in the change. Those chemical processes in which a condition of equilibrium is attained, *i.e.*, in which the chemical reaction proceeds simultaneously in two opposite directions, are most suited for the study of chemical force. The special class of actions chosen by the authors consisted of those in which a soluble and an insoluble salt divide two acids between themselves, *e.g.*, the decomposition of K_2SO_4 by $BaCO_3$, and the reverse decomposition of K_2CO_3 by $BaSO_4$.

The following general expression was deduced from a large number of experimental results:—

When two bodies, A *and* B, *decompose one another with production of two new bodies*, A′ *and* B′, *the chemical force with which* A *and* B *mutually act on one another is measured by the amounts of* A′ *and* B′ *produced in a unit of time.*

Active mass of a substance is defined as the amount of that substance in the unit-volume of the chemical system within which the chemical change proceeds.

The chemical force with which two bodies, A *and* B, *react on one another is equal to the product of the active masses of these bodies multiplied by the coefficient of affinity.*

The coefficient of affinity is dependent on the chemical nature of the reacting bodies and on the temperature.

If A and B are decomposed into A′ and B′, and conversely A′ and B′ into A and B, *equilibrium is established when the chemical force exerted between* A *and* B *is equal to that exerted between* A′ *and* B′.

Let the active masses of A and B be represented by p and q and those of A′ and B′ by p' and q' respectively, and let the coefficient of affinity in the first action be k and that in the second k', then the conditions of equilibrium are expressed by the formula

$$kpq = k'p'q'.*$$

This formula supposes that the action of secondary forces is overlooked. The law of mass action formulated above was applied in the authors' "Études" to the cases of chemical action already cited and also to the case of ether formation.

In the present paper they apply this law to many classes of reaction, and also endeavour to develop the physical significations thereof, with the object of establishing the general applicability of the law.

Reactions which result in the permanent formation of chemical bodies different from those already present are regarded by the authors as *incomplete reactions;* when, on the other hand, reverse action begins and is carried to completion, *i.e.*, when the original

* The expression kpq represents the amounts of A and B converted into A′ and B′ in unit time.

condition of equilibrium is re-established, we have what they regard as a *complete reaction.* Various circumstances which tend to render chemical reactions incomplete are enumerated: the principal are, removal of the products of the first part of the reaction from the sphere of action, or the initiation of secondary changes among these products; the maintenance of a temperature such as prevents the second portion of the reaction from proceeding; the existence of values for the affinity coefficients such that equilibrium is established by the presence of very small quantities of the reacting substances.

The theory of mass action, proposed by the authors when secondary forces are not considered, is briefly as follows:—In considering such a chemical change as $A + B = A' + B'$, $A' + B' = A + B$, it is necessary to take into account the vibratory movements of the molecules and of the atoms of A and B. Let A be a compound molecule consisting of the atoms α and γ, and B a compound molecule consisting of the atoms β and δ; let the atoms α and γ vibrate to and fro within A, and β and δ vibrate within B; when α and β are respectively at the extreme outer limits of their vibration, let A and B come within the sphere of each other's action: A and B are then decomposed with formation of A′ and B′, which are made up of atoms $\alpha\beta$ and $\gamma\delta$ respectively. So long as the decompositions of A and B and the decompositions of A′ and B′ are equal in number in a unit of time a condition of equilibrium is maintained.

Let the number of molecules of A and B in unit volume be p and q respectively, and of these let the numbers which come within the sphere of each other's action in unit time be ap and bq respectively: then the frequency of encounters resulting in decomposition between the molecules will be expressed by the product $apbq$, and the velocity with which the production of new molecules proceeds will be

$$\phi apbq = kpq.$$

when ϕ is a coefficient of velocity and $k = \phi ab$.

This equation may be made general for a system containing any number of reacting substances.

The velocity of formation of an *addition-compound* consisting of α molecules of A, β molecules of B, and γ molecules of C, is expressed by the equation $\phi apap \ldots bqbq \ldots crcr = kp^{\alpha}q^{\beta}r^{\gamma}$; where p, q, and r represent the number of molecules of A, B, and C respectively in a unit-volume of the system; a, b, and c the coefficients of A, B, and C respectively, and where k is the product of all the coefficients.

a, b, c are doubtless dependent on the temperature as also on the nature of A, B, and C; ϕ is also dependent on the temperature, but the exact nature of this dependence can be determined only by experiment.

Having determined the velocity of formation of new molecules, it is only necessary to make this equal to the velocity of re-formation of the original molecules, in order to obtain the condition of equilibrium of the reacting systems.

The absolute velocity of the chemical change is evidently equal to the difference between the velocities of the direct and of the reverse actions. From this the time required for the completion of the change may be calculated.

If dilute solutions are employed, the action of secondary forces may be overlooked without falling into grave error.

The authors' theory is applied to a large series of reactions. Among the more important are *systems consisting of four soluble compounds.*

If in such a reaction as $A + B_1 = A_1 + B$, a and b are used to express the affinity coefficients of A and B and a_1 and b_1 the coefficients of A_1 and B_1 respectively, and p, p_1, q and q_1 respectively express the amounts of A, B_1, A_1, and B_1 (these amounts being represented, for the sake of simplicity, by equivalents), then the following equation holds—

$$k\frac{p}{q} = k_1\frac{p_1}{q_1} \qquad \left(k = \frac{a}{b} : k_1 = \frac{a_1}{b_1}\right).$$

From the results of experiment the proportion $\frac{k}{k_1}$ may be easily deduced. Having determined the proportion $k_1 : k$ for the system A, B, A_1, B_1 the proportion $k_2 : k$ may be determined for a new system, A, B, A_2, B_2, and if k be then taken as $= 1$, the *relative value* of k_1, k_2, &c., in reference to the pair of bodies, A B, may be calculated. By tabulating these values it becomes possible to calculate the conditions of equilibrium for any two pairs of substances occurring in the table. Thus, if the conditions of a system, A_1, A_2, B_1, B_2, are to be calculated, the equation is $k_1\frac{p_1}{q_1} = k_2\frac{p_2}{q_2}$: the values of k_1 and k_2 are found from the table.

TABLE I.—*Relative Values of k.*

A.		B.	k.
Hydrochloric acid....	HCl	NaCl	1
Nitric ,, ...	HNO_3	$NaNO_3$	1
Sulphuric ,, ...	$\frac{1}{2}(H_2SO_4)$	$\frac{1}{2}(Na_2SO_4)$	0·25
Oxalic ,, ...	$\frac{1}{2}(H_2C_2O_4)$	$\frac{1}{2}(Na_2C_2O_4)$	0·0676
Phosphoric ,, ...	H_3PO_4	NaH_2PO_4	0·0625
Tartaric ,, ...	$\frac{1}{2}(C_4H_6O_6)$	$\frac{1}{2}(C_4H_4Na_2O_6)$	0·0025
Citric ,, ...	$\frac{1}{3}(C_6H_8O_7)$	$\frac{1}{3}(C_6H_5Na_3O_7)$	0·0025
Acetic ,, ...	$C_2H_4O_2$	$C_2H_3NaO_2$	0·0009
Boric ,, ...	$\frac{1}{2}HBO_2$	$NaBO_2$	0·0001

TABLE II.

A.	B.	k.
Hydrochloric acid	Metallic chloride	1
Sulphuric ,,	,, sulphate	0·25

The metal may be potassium, sodium, or ammonium.

TABLE III.

A.	B.	k.
Hydrochloric acid	Metallic chloride	1
Sulphuric ,,	,, sulphate	0·5

The metal may be Mg, Mn, Fe, Zn, Co, Ni, Cu.

Table IV.

A.	B.	k.
ClR''	$\frac{1}{2}(SO_4R_2'')$	1
ClR'''	$\frac{1}{2}(SO_4R_2''')$	2

$R'' =$ metal of Table II; $R''' =$ metal of Table III.

The authors deduce an equation by means of which it becomes possible to calculate a limiting value for the velocity of the reaction: this limiting value is theoretically attained at the end of an infinite time, but practically very soon after the beginning of the reaction.

The special systems of four soluble compounds considered are—

I. Acetic acid, water, ether, and alcohol.

II. Ferric chloride, hydrochloric acid, ferric oxide, and water.

III. Nitric acid, sodium nitrate, sulphuric acid, and sodium sulphate.

Systems consisting of two soluble and two insoluble compounds, are next considered.

In the case of insoluble compounds the active mass of the compound does not necessarily decrease in the same proportion as the total amount of the substance present. Increase of the absolute amount of an insoluble substance does not increase the active mass to any sensible extent.

In the systems now under consideration it is shown that, in a state of equilibrium, the proportion between the amounts of the two soluble compounds is always the same, the mass of the insoluble substances being unchanged throughout the experiment.

The special cases considered are:—

I. Barium sulphate, potassium sulphate, barium carbonate, and potassium carbonate. Four-fifths of the total potash exists as carbonate, and one-fifth as sulphate.

II. Barium sulphate, sodium sulphate, barium carbonate, sodium carbonate.

The special case illustrative of *systems consisting of three soluble and one insoluble compound*, which is considered is, hydrochloric acid, oxalic acid, calcium chloride, and calcium oxalate.

In the case of *systems consisting of an indefinite number of soluble compounds*, it is shown that a formula may be deduced from the law of mass action, which enables the results of the reaction to be calculated.

The truth of the hypothesis—itself a deduction from fundamental dynamical principles—that, when several chemical actions proceed simultaneously in the same liquid, the velocity of each reaction is independent of the others—is assumed in these calculations.

In the case of *systems consisting of two insoluble, and an indefinite number of soluble compounds*, the statement is deduced from equations and confirmed by experiments, that, each pair of soluble compounds reacts with the pair of insoluble compounds independently of the nature of the bodies already in solution.

The special case considered is a system consisting of barium sulphate, potassium sulphate, sodium sulphate, barium carbonate, potassium carbonate, and sodium carbonate.

Formulæ are deduced which enable the condition of equilibrium to be calculated for *systems consisting of soluble and gaseous compounds when the latter are absorbed by the solution.* The special case considered is chlorine, oxygen, hydrochloric acid, and water. Similarly, formulæ are deduced applicable to *systems consisting of gaseous bodies which result from the dissociation of a solid compound.* Horstman's results on the dissociation of ammonium carbonate (*Annalen*, **187**, 1877, and this Journal 1877 [i], 433) are shown to agree with the results required by the authors' equations.

Finally, the general law of mass action is shown to be applicable to the case of *systems consisting wholly of gaseous compounds.* Various cases of dissociation are here considered, more especially those in which only the dissociated compound is present, *e.g.*, Naumann's results with N_2O_4 and NO_2 (*Ber.*, **10**, 2045, and this vol., p. 195), those cases in which one of the constituents of the dissociated compound is present in excess, *e.g.*, Lemoine's results with HI and excess of H or I (this Journal, Abst., 1878, 265); and, lastly, those cases in which neither of the constituents is present in excess (Lemoine, *loc. cit.*). M. M. P. M.

Note by Abstractor.—In the paper of which the foregoing is an abstract, reference is made to an important communication by Ostwald (*J. pr. Chem.* [2], **16**, 385), in which the relative affinities of various acids for bases are determined by measuring the changes in volume undergone by aqueous solutions of these acids when neutralised by aqueous solutions of the bases in question (see also this Journal, 1878, Abstr., p. 196, and this vol., p. 348).

In his first paper, Ostwald shows that, very probably, the relative affinity of acids for bases is a constant number, independent of the base, and conversely, that the relative affinity of bases for acids is also independent of the acid. From this general statement, Ostwald deduces the result, that the force of affinity acting between an acid and a base is the product of a specific coefficient of affinity for the acid, and a specific coefficient of affinity for the base.

If this statement be accepted as of general application, then it becomes possible to give a very simple expression for the affinities which come into play in the formation of salts. Having determined the relative affinities of all acids in reference to one base, and of all bases in reference to one acid, and taking the affinity of *this* acid for *this* base as 1, the values found may be arranged in the form of a table as follows:—

	$\phi(A)$.	$\phi(A')$.	$\phi(A'')$.	$\phi(A''')$.
$\psi(C)$				
$\psi(C')$...				
$\psi(C'')$...				
$\psi(C''')$..				

The absolute affinity of an acid A for a base C is a function of both; this function is a product of two factors, one of which contains only A, the other only C.

$$f(A,C) = \phi(A).\psi(C).$$

The product of any number contained in the horizontal column, ψ (C), with the number contained in the corresponding vertical column, ϕ (A), would express the magnitude of the affinity acting between the given acid and base, f (A, C), stated in empirical units.

Inasmuch as the *relative affinity of acids for bases is independent of temperature*, the table might be extended in a third direction in space, which direction would contain the *influence of temperature on the absolute affinity;* the nature of this influence has yet to be determined.

M. M. P. M.

A Calorimetric Method. By F. Stohmann (*J. pr. Chem.* [2], **19**, 115—149).—The author has carried out a series of experiments with the calorimeter of Lewis Thompson described by Frankland (*Phil. Mag.* [4], **32**, 182). The results were far from satisfactory. The main causes of error are: the cylinder which contains the water parts with or absorbs heat during the experiment, according to the temperature of the surrounding atmosphere; the combustion tube is oxidised during the operation, and heat is thus evolved; after the combustion, a considerable quantity of potassium chloride remains undissolved; the combustion takes place with almost explosive violence; large quantities of undecomposed potassium chlorate and unburned substance remain in the combustion cylinder when the operation is finished.

The author has constructed a new calorimeter after the model of Lewis Thompson's. The water cylinder is made of brass, silvered on the outside, and covered with several layers of thick flannel; the combustion cylinder is made of platinum, the bottom consisting of a gold platinum alloy; this cylinder is pierced with several holes to admit of the entrance of water, whereby the complete solution of the potassium chloride produced during the process is ensured. Before the combustion these holes are stopped with a weighed quantity of fine silk paper. The intensity of the combustion is diminished by mixing a weighed quantity of powdered pumice stone with the combustion mixture. In every instance a considerable amount of potassium chlorate remained undecomposed: the amount of potassium chloride in solution was determined after each experiment, and thus the quantity of chlorate which had been decomposed was found. The quantity which should have been decomposed in order thoroughly to burn the weight of substance taken was calculated; if in any experiment less than 99 per cent. of the calculated amount of potassium chloride was actually produced, that experiment was rejected.

The method of using the instrument is detailed with great minuteness, and the corrections which it is necessary to make are very fully considered. For these details reference must be made to the original paper. The final correction which must be introduced into each calculation is shown to agree very well with the number obtained by Frankland from his experiments.

The author's method is not applicable to substances which are readily volatile and give out but little heat on combustion. Nor can the heat of combustion of urea and hippuric acid be correctly determined by this process, inasmuch as oxides of nitrogen and nitric acid are produced in large quantity from these compounds. If, however, a known amount of some substance having a high (known) heat of combustion, be mixed with the volatile body to be burned, or with the urea or hippuric acid, then the heats of combustion of these bodies can be correctly determined. M. M. P. M.

On New Phenomena shown by Gases. By A Mitscherlich (*Chem. Centr.* [3], 1878, 828—829).—The ignition point of hydrogen depends on the following conditions, and is therefore variable.

1. *The Shape of the Vessel.*—In a cylinder the ignition point becomes lower as the diameter of the cylinder, or the surface in contact with the gas, is diminished. For every millimeter decrease of diameter the ignition point becomes about 6·6° lower. The diameter was varied from 1—12 mm.; in narrower tubes disturbing effects were noticed, and in broader ones the thickness of glass requisite to resist the powerful explosion caused irregularity.

2. *The nature of the surface* had also considerable influence on the ignition point. If the glass surface is coated with phosphoric acid the ignition point is much lower, whilst if the glass has been treated with hydrofluoric acid, the ignition point is considerably raised: these alterations of temperature exceed 40° C.

3. *The proportion of oxygen present* affects the ignition point, apparently in proportion to the alteration it produces in the sp. gr. of the mixture: if the sp. gr. is lessened by decreasing the proportion of oxygen, the ignition point is raised, whereas it is lowered by increasing the proportion of oxygen and the sp. gr. of the mixture: the alteration thus producible exceeds 50° C. Should other indifferent gases be also present, their effect depends on their nature and proportion. Carbonic and sulphurous anhydride and others tend to raise the ignition point as hydrogen does; whilst ozone, nitrogen, and nitrous oxide tend like oxygen to depress the ignition point. Sulphurous anhydride produces an elevation of ignition point of over 20° C., and nitrous oxide a depression of over 80° C. The variation in the proportion of these gases produces an effect similar to variation in the proportion of hydrogen and oxygen.

4. *Pressure* produces a very regular effect on the ignition point, every decrease of pressure equivalent to 1 mm. of mercury producing a fall in the ignition temperature of 0·18° C.; this law is not interfered with by altering the form of the vessel or the proportions and natures of the gases present. The effect of a pressure greater than that of the atmosphere could not be tried, on account of the violence of the explosion under the increased pressure.

In comparing the results here detailed with what was previously known, the author notes that increased surface was found to lower the ignition point, as when spongy platinum is made to ignite a mixture of hydrogen and oxygen, but in this particular case the influence is due to absorption on the surface itself, whereas in the author's

experiments the surface acts only at a distance from the bulk of the gases. Further, it would have been anticipated that the admixture of indifferent gases would always raise the ignition point by separating the molecules. Experiments with salts containing loosely combined oxygen and sulphur, and ignition produced by compression of air, would lead us to think that increase of pressure lowered the ignition point, whereas it has the reverse influence. It appears from the author's experiments that the increase of surface of the vessel tends to hinder chemical action: it is therefore probable that the surface will have some influence in the experiments for determining the expansion of gases by heat and their specific heat. F. C.

Researches in Thermometry. By E. J. Mills (*Phil. Mag.* [5], 662).—If an old thermometer is immersed in boiling water, the zero point descends, but attains its original position if kept for two or three years at the ordinary temperature. If x represent the time in months, y the remaining depression, and A and B the total depression, the equation to the ascent will be between 0 and 100°—

$$y = A\alpha^x + B\beta^n.$$

The author also mentions that although the zero falls when the thermometer is heated to 100°, in the case of lead glass instruments it rises if the temperature be raised above 120—150°; that the maximum difference of the mercurial and the air thermometer lies at about 33°; that the effect of external pressure on a thermometer bulb varies directly as the pressure; that every thermometer has individual characteristics not susceptible of general correction; and lastly, that standard temperatures may be readily obtained by means of the melting points of certain substances. F. D. B.

Relation between the Melting Points of the Elements and their Coefficients of Expansion by Heat. By T. Carnelley (*Deut. Chem. Ges. Ber.*, **12**, 439—443).—From certain theoretical considerations, the author concludes that the coefficients of expansion by heat of the elements is related in such a manner that as the former increases the latter decreases. In the case of 31 elements compared, there are five exceptions, viz.: arsenic, antimony, bismuth, tellurium, and tin. The first three, which belong to the same group, exhibit however, this relationship amongst themselves. P. P. B.

Heat Absorption attending the Solution of Potassium Chloride in Water. By V. Rechenberg (*J. pr. Chem.* [2], **19**, 143—145).—The calorimeter described by Stohmann (this vol., p. 586) was employed. The mean value of S, *i.e.*, thermal effect for solution of one molecule potassium chloride, was found to be = — 4421 or — 4434 heat-units, according as the number of Thomsen or that of Winkelmann for the specific heat of the aqueous solution of the chloride, was adopted.

$S = \frac{s}{g}(74{\cdot}6)$, where s = thermal effect for g grams. The heat-unit employed equals amount of heat required to raise the temperature

of 1 gram of water through 1°. The value found for S agrees well with that calculated from the data of Thomsen and A. Winkelmann.

M. M. P. M.

Heat Developed by Contact of Water with Anhydrous Sodium Sulphate. By L. C. de Coppet (*Deut. Chem. Ges. Ber.*, **12**, 248—249).—When anhydrous sodium sulphate is brought into contact with water, a rise in temperature, sometimes above 100° C., takes place (*Compt. rend.*, **79**, 167). Thomsen (*Ber.*, **11**, 2042) explains this phenomenon by supposing that a hydrate, $Na_2SO_4.H_2O$, is formed.

The author considers this theory to be erroneous, for when a solution of Glauber's salt, saturated at 35—40°, is slowly heated in closed vessels, *anhydrous* sodium sulphate is deposited. It is besides an open question whether the crystalline powder which separates when ordinary Glauber's salt crystals ($Na_2SO_4.7H_2O$) are melted at 33°, does or does not contain water.

Ch. B.

Decomposition of Haloïd Acids by Metals. By Berthelot (*Bull. Soc. Chim.* [2], **31**, 302—309).—By arranging the metallic chlorides according to their heats of formation, a classification of the metals, very different from the ordinary classifications, is obtained. According to this list, the heat of formation of hydrochloric acid, + 22 thermal units, is exceeded by that of all the metals with the exception of gold, and therefore it ought to be decomposed by all these metals. But as the relation between hydrogen and hydrochloric acid which are gaseous bodies is not the same as exists between a metal and its chloride which are solid bodies, it is necessary to reduce the former to the solid state by adding to its heat of formation the difference between the heats of sodification of hydrochloric acid and hydrogen, or to reduce the latter to the gaseous state by subtracting from its heat of formation, the difference between the heats of vaporisation of the chloride and of the metal. By these calculations it is found that the heat of formation of lead chloride is + 41·4 cal.; cuprous chloride, 33·1; mercurous chloride, 40·9; and silver chloride, 29·2; whilst that of palladium in presence of potassium chloride is 26·3, and of platinum under the same circumstances 22·6. It is therefore evident that all metals, with the exception of platinum and probably palladium, should decompose hydrochloric acid, with disengagement of hydrogen. That this is the case with the metals of the first three sections is well known. The action between hydrochloric acid and lead and copper can easily be proved even in the cold, but between mercury and hydrochloric acid the action takes place only at a high temperature; on sealing in a tube gaseous hydrochloric acid and metallic mercury, and heating for some time at 500—600°, a slight decomposition sets in, a small quantity of hydrogen is set free, and a trace of mercurous chloride is formed. By passing hydrochloric acid gas charged with the vapour of mercury through a tube heated between 800° and 1000°, hydrogen is set free, and mercurous chloride condenses in the cool part of the tube. This shows also that mercurous chloride exists in the gaseous state at 800°. There is little doubt, however, that dissociation does take place, which accounts for the large quantity of hydrochloric acid existing in presence of metallic mercury. In this case, therefore, there are two

inverse reactions taking place; the mercury decomposes the hydrochloric acid forming mercurous chloride which is dissociated, and the chlorine unites with the free hydrogen, forming hydrochloric acid. These two inverse reactions are possible because they are both effected with disengagement of heat. Silver acts on gaseous hydrochloric acid between 500° and 550°, forming a sub-chloride, which coats the surface of the metal and hydrogen is set free; when the quantity of hydrogen set free is large, the inverse reaction sets in.

Neither palladium nor platinum decomposes hydrochloric acid at a temperature of 550°.

On examination of what takes place when the acid is dissolved in water, it is found that if sufficient water is added to form a definite hydrate, the heat of formation of the hydrate is +39 cal., which is exceeded by the alkali-metals, the metals of the alkaline earths, and the metals of the iron group; lead and tin are on the limit, and silver, copper, and mercury are less. By adding less water or raising the temperature, the liquid contains some anhydrous acid and possibly an intermediate heat of formation; this explains why concentrated hydrochloric acid attacks lead and copper.

Analogous reactions take place with sulphuretted hydrogen. Silver and mercury decompose it at about 500°, with formation of metallic sulphide and disengagement of hydrogen; at that high temperature, the hydrogen produces the inverse reaction. Copper completely decomposes sulphuretted hydrogen at that temperature, and even slightly in the cold; at 100°, hydrogen is rapidly evolved, and at 550°, the inverse reaction sets in.

The conformity between theory and practice is more striking with hydriodic and hydrobromic acid: for not only the alkali-metals, the metals of the alkaline earths, and the metals of the iron group are attacked by them in the cold, but also lead, silver, and mercury, the difference between the heats of formation of the acids and their compounds with these metals being greater than in the case of hydrochloric acid; thus—

H + Br gas.....	+13·5	H + I gas	− 0·8
Pb + Br ,, ...	+38·5	Pb + I ,, ...	+26·4
Cu_2 + Br ,, ...	+30·0	Cu_2 + I ,, ...	+21·9
Hg_2 + Br ,, ...	+39·2	Hg_2 + I ,, ...	+29·2
Ag + Br ,, ...	+27·7	Ag + I ,, ...	+19·7

The decomposition of these acids therefore should be more readily accomplished, which is the case.

Hydrobromic acid is slowly decomposed by mercury in the cold, and also by silver; silver bromide, however, is only partially decomposed by hydrogen at 550°, and silver iodide resists the action of hydrogen completely. L. T. O'S.

Determination of the Atomic Heat of Hydrogen in its Combination with Palladium. By M. Beketoff (*Bull. Soc. Chim.* [2], **31**, 197—199).—The author's determinations were on the assumption that hydrogen and palladium retain their original specific

heats in combination, as is the case with the metals of alloys generally. A ribbon of palladium, more than a meter in length, was coiled into a helix and heated until covered with a considerable coating of oxide; the oxide was then reduced by a current of dry hydrogen, and the occluded hydrogen expelled by a current of carbonic anhydride. The perfectly pure and porous metal thus obtained was able to absorb about 710 times its volume of hydrogen. The occlusion was effected at 100°, and the weight of alloy thus obtained determined in a sealed tube in an atmosphere of hydrogen. The alloy was again heated at 100° for some time, and plunged into the water of a calorimeter; the saturated palladium lost no gas during this immersion. The quantity of hydrogen occluded by the metal at the above temperature was determined by heating the saturated palladium in a tube with sodium bicarbonate; the occluded hydrogen was expelled by the carbonic anhydride, and the mixed gases were received in graduated tubes and analysed.

The value deduced for the atomic heat of hydrogen by this method, using the ordinary equation, was 6·2. This is very near the atomic heat of silver (6·16) and copper (6·02), the metals which show the greatest analogy with hydrogen. J. M. H. M.

Thermo-Chemistry. Combination of Carbonic Oxide with the Elements. By Berthelot (*Bull. Soc. Chim.*, [2], **31**, 227—229).—Carbonic oxide behaves like an element in forming addition compounds, as oxide, chloride, sulphide, &c. It appeared interesting to determine the heat developed in these combinations.

Carbonic oxide with chlorine. Chlorocarbonic acid gas was absorbed by a weak solution of potash contained in a calorimeter; the heat disengaged was + 112·2 kilogram-degrees for $COCl_2$ = 99 grams, from which is deduced—

$COCl_2$ gas + H_2O + water = CO_2 dissolved + 2HCl dissolved	+64·6
C (diamond) + O + Cl_2 = $COCl_2$ gas	+44·6
CO + Cl_2	+18·8

The author wished to make a similar determination for bromocarbonic acid (a substance whose formation was announced in 1863 by Schiel), but on attempting to prepare this body by the action of bromine on carbonic oxide in sunlight, he found no trace of combination even after several months' exposure.

Carbonic oxide with sulphur. The heat disengaged by the action of potash on carbonyl sulphide gas was + 48·08 units for COS = 60 grams, whence—

COS gas + H_2O + water = CO_2 dissolved + H_2S dissolved	+20·2
C (diamond) + O + S solid = COS gas	+19·6
CO + S solid = COS gas	− 3·1
CO + S gas = COS gas	− 3·6

This negative number corresponds with the feeble stability of carbonyl sulphide. The transformation $2COS = CS_2 + CO_2$ disengages about + 40·0 heat units.

Carbonic oxide with oxygen. According to the previous experiments of the author

$$CO + O = CO_2 \ldots\ldots\ldots \quad +68{\cdot}2.$$

Comparing CO with hydrogen, we have—

$CO + O = CO_2$..	+68·2	$H_2 + O = H_2O$ gas	+59·0
$CO + S$ gas $= COS$	− 3·6	$H_2 + S$ gas $= H_2S$	+ 7·2
$CO + Cl_2 = COCl_2$	+18·8	$H_2 + Cl_2 = 2HCl$	+44·0

The order of the numbers is the same in both cases; COS and $COCl_2$ are, however, very much less stable than the corresponding hydrogen compounds, and the heat evolved in their formation is much less also. J. M. H. M.

Inorganic Chemistry.

Formation of Ozone by Hydrocarbons. By J. Schiel (*Deut. Chem. Ges. Ber.*, **12**, 507—508).—When metallic sodium, potassium, and thallium are preserved under benzene or petroleum in stoppered bottles, the bright surface of the metals rapidly tarnishes. The author supposes that ozone is formed by the action of the hydrocarbon on the air contained in the bottle, and that the ozone oxidises the metallic surfaces. W. C. W.

Hydrogen Peroxide. By E. Schöne (*Liebig's Annalen*, **196**, 58—74).—The following results directly contradict the observations of Schönbein (*J. pr. Chem.*, **93**, 38).—Thallic oxide is precipitated on the addition of hydrogen peroxide to an excess of thallium monoxide. When a neutral solution of hydrogen peroxide is added to thallic hydroxide, oxygen is evolved, but thallium monoxide is not formed; if the solution is acid, mutual reduction takes place: $2H_2O_2 + Tl_2O_3.H_2O + H_2SO_4 = 2O_2 + Tl_2SO_4 + 4H_2O$.

The coloration which ozone produces on paper moistened with thallious hydrate solution, is bleached by an acid but not by a neutral solution of hydrogen peroxide. Thallium paper is turned brown on exposure to the vapour of hydrogen peroxide: hence the presence of ozone in the atmosphere cannot be detected by this reagent.

Manganese and lead dioxides decompose a neutral solution of hydrogen peroxide, without undergoing any change themselves.

W. C. W.

Hydrogen Peroxide. By E. Schöne (*Liebig's Annalen*, **196**, 239—258).—In the mutual decomposition which takes place when ozone is brought in contact with an aqueous solution of hydrogen peroxide, each substance loses the same volume of oxygen. The increase in volume of the gas is equal to the sum of the volumes of oxygen lost by the ozone and by the hydrogen peroxide. These results confirm the accuracy of Brodie's experiments (*Phil. Trans.*, **162**, ii, 454).

Hydrogen peroxide is decomposed by chlorine-water, with evolution of oxygen, one molecule of oxygen being evolved for each molecule of chlorine which takes part in the reaction, $H_2O_2 + Cl_2 = 2HCl + O_2$. It is, however, possible that only half the oxygen is derived from the hydrogen peroxide, the other half being due to the decomposition of a molecule of water by the chlorine, *e.g.*:—

$$H_2O\overline{|O + O|}\overline{|H_2 + Cl_2|} = H_2O + O_2 + 2HCl.$$

W. C. W.

Action of Oxalic Acid on Chlorates, Bromates, and Iodates. By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 299—301).—A boiling supersaturated aqueous solution of oxalic acid decomposes solutions of chlorates, bromates, and iodates, with evolution of chlorine, bromine, and iodine respectively. In the case of potassium chlorate, a large quantity of chlorine is evolved, but still a considerable quantity of the chlorate is reduced to chloride.

With potassium bromate a similar reaction takes place, but the proportion of the bromine evolved to the bromide formed is greater than between the chlorine and chloride in the case of the chlorate.

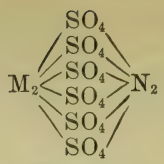
Iodates evolve all their iodine in the free state, no traces of iodides being formed.

In the case of mixtures of these bodies, the chlorates are first decomposed, then the bromates, and finally the iodates, that which is attacked first being completely decomposed before the others are acted on. It was observed that the steam accompanying the gas evolved expelled all traces of it before vapours of the second halogen made their appearance. This can be distinctly seen, as there is a certain interval between the two reactions, it being necessary in some cases to add some oxalic acid to start it again.

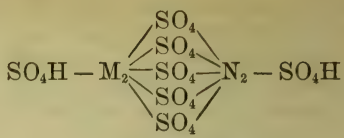
These reactions afford the means of testing for the presence of chlorine and iodine in commercial bromine, and also the purity of bromides and bromates. The bromine is dissolved in a slight excess of concentrated potash, and treated with oxalic acid. Bromides are oxidised to bromates by means of chlorine, and then treated with oxalic acid, and bromates are treated directly with oxalic acid. L. T. O'S.

Researches on the Sulphates. By A. Etard (*Bull. Soc. Chim.* [2], **31**, 200—204).—In this paper the author describes a number of double sesquisulphates, the formation and constitution of which he represents in the following manner:—

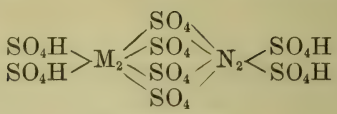
When a sesquisulphate, $(M_2)^{vi}(SO_4)_3$, is dissolved in concentrated sulphuric acid, we may suppose the formation of an acid salt, according to the equation $M_2(SO_4)_3 + 3H_2SO_4 = M_2(HSO_4)_6$. When the temperature of a solution containing two such salts is progressively raised to nearly the boiling point, 2 molecules of the bisulphates may part with 6, 5, or 4 molecules of H_2SO_4, to give the following derivatives:—



Neutral salt.



1st acid salt.



2nd acid salt.

Preparation.—The sesquisulphates to be combined are dissolved in a little cold water, a large excess of concentrated sulphuric acid is added, and the solution heated until it deposits a crystalline precipitate; this is collected in a funnel whose neck is stopped with a plug of glass wool, drained by the filter-pump, washed successively with pure sulphuric acid, anhydrous acetic acid, and alcohol, and then dried in the oven. Instead of sulphates, salts of the sesquioxides with volatile acids may be employed.

For the chromium compounds, 2 molecules of chromic acid may be used instead of a chromic salt. Manganese requires particular treatment, on account of the difficulty of obtaining salts of the sesquioxide; instead of a manganic salt, 2 molecules of a manganous salt are dissolved in the sulphuric acid, together with the sesquisulphate of the other metal, and as soon as a precipitate begins to form on heating the solution, nitrosulphuric acid is added in small portions, until the liquid assumes a violet colour, and deposits a precipitate, which contains the manganese in the state of sesquioxide. This oxidation succeeds only in the presence of another sesquisulphate.

Acid Sesquisulphate of Iron and Alumina, $Al_2(SO_4)_6Fe_2.SO_4H_2$.—Minute white hexagonal plates, insoluble in water, which, however, slowly decomposes it. On heating, it loses H_2SO_4, and becomes the *neutral salt*, $Al_2(SO_4)_6Fe_2$, which is also obtained by heating the sulphuric solution to a higher temperature; it is white, and insoluble in water or acids.

Acid Sesquisulphate of Iron and Chromium, $Cr_2(SO_4)_6Fe_2.SO_4H_2$.—Crystalline, yellowish, and insoluble. *Neutral salt*, $Cr_2(SO_4)_6Fe_2$, insoluble.

Sesquisulphate of Iron and Manganese, $Mn_2(SO_4)_6Fe_2$.—Crystalline, insoluble, of a fine green colour (similar to *Rinmann's green*); it decomposes hydrochloric acid, with disengagement of chlorine.

Acid Sesquisulphate of Chromium and Manganese, $Cr_2(SO_4)_6Mn_2.SO_4H_2$.—Crystalline, chocolate-brown, soluble in water with decomposition; disengages chlorine from hydrochloric acid.

In preparing this salt, the sulphuric solution must be withdrawn from the heat *before* a precipitate forms, and allowed to cool. By continuing to heat, the *neutral salt*, $Cr_2(SO_4)_6Mn_2$, is obtained; it is yellowish-green, crystalline, and is attacked by hydrochloric acid, with disengagement of chlorine.

Acid Sesquisulphate of Chromium and Aluminium, $Cr_2(SO_4)_6Al_2.SO_4H_2$. —Crystalline, pale green; heated in the sulphuric solution, it gives the *neutral salt*, $Cr_2(SO_4)_6Al_2$.

Sesquisulphate of Aluminium and Manganese, $2Al_2(SO_4)_3.Mn_2(SO_4)_3$. —Sky-blue crystalline sand, insoluble in water, which decomposes it very slowly; soluble in hydrochloric acid, with disengagement of chlorine.

These salts are for the most part insoluble, although some of them contain as much as 80 per cent. SO_4.

If, instead of combining the sesquisulphates of two different metals, a double quantity of the same sesquisulphate be taken, we produce a class of bodies already known. These are the *insoluble* modifications of ferric, aluminic, and chromic sulphates. The best known of these is the red chromic sulphate, a neutral salt according to some authors, acid according to others. This rose-grey salt (bright rose on heating), is extremely stable, and insoluble in acids; its formula is $Cr_2(SO_4)_6Cr_2$. Another chromic sulphate has the formula $Cr_2(SO_4)_6Cr_2.SO_4H_2$; this is the one to which Traube assigned the formula

$$2(Cr_2O_3.3SO_3).SO_4H_2.$$ J. M. H. M.

Iodated Potassium Iodide. By A. Guyard (*Bull. Soc. Chim.* [2], **39**, 297—299).—Iodated potassium iodide, consisting of 3 parts of iodine dissolved in a solution containing 4 parts of potassium iodide, contains potassium di-iodide, KI_2, a compound analogous to manganese sesquichloride. When metallic salts are added to this solution, either a mixture of an ordinary iodide and free iodine is precipitated, or an iodide corresponding to a di-iodide, according to the metal employed. Thus with lead acetate a dark coloured precipitate is formed, which does not evolve iodine, even when heated to high temperatures, and has the formula PbI_4.

If less than 3 parts of iodine be employed, the solution consists of a mixture of potassium iodide and potassium di-iodide, as is seen from the action of a lead salt, which gives first a precipitate of lead di-iodide, and the filtrate from this gives a yellow precipitate of lead iodide.

Mercurous nitrate gave a scarlet precipitate of mercuric iodide, but with mercuric chloride a dark precipitate is formed, consisting of a mixture of mercuric iodide and free iodine.

A concentrated solution of stannous chloride gives a yellowish-red precipitate of SnI_4, whilst silver nitrate gives a precipitate of silver iodide and free iodine.

When added to methyl alcohol, made slightly alkaline, potassium di-iodide produces a voluminous precipitate of iodoform, whereas pure ethyl alcohol under the same circumstances does not yield a trace. This reaction permits us to distinguish between the two alcohols, and to a certain degree to test the purity of ethyl alcohol.* L. T. O'S.

Preparation of Potassium Nitrite. By H. Müller and C. Pauly (*Arch. Pharm.*, **14**, 245—252).—After reviewing the various

* The author appears to be quite unaware that the subject has been already investigated by G. S. Johnson (this Journal, 1877, 249, and 1878, Transactions, 183 and 397), whose results are not in accord with some of the statements in this paper. —C. E. G.

processes which have been proposed for the preparation of potassium nitrite, the author gives the preference to Persoz's method (*Dingl.*, **173**, 75). The reason why it is so seldom employed is the difficulty and cost of preparing the finely divided copper by the dry distillation of copper acetate, but this objection has been overcome by the use of the copper precipitate, obtained by decomposing a solution of copper sulphate with zinc-dust. The latter is made into a paste with water, and added in portions of 10—15 grams at a time to a moderately concentrated cold solution of copper sulphate. Much heat is developed by the reaction, so that it is necessary to cool, in order to avoid decomposition of the copper salt by the zinc oxide always present in zinc-dust. When the solution becomes almost colourless, the zinc must be added cautiously and gradually, until there is a slight excess, and the whole of the copper is precipitated. After decanting the solution of zinc sulphate and washing the precipitate once with boiled water, it is treated with dilute hydrochloric acid, to remove zinc oxide and traces of metallic zinc. As the finely divided copper oxidises rapidly, it must be washed in the cold with boiled water, excluding the air as far as possible, and after draining off the water, it is mixed in the moist state with finely powdered potassium nitrate (10 parts nitrate to every 25 of copper sulphate originally taken), and dried rapidly with constant stirring. The mixture is then projected in small portions at a time into a crucible heated to low redness; the reaction is complete as soon as the fused mass becomes pasty, when a fresh portion may be added, stirring occasionally with an iron spatula. The mass is removed from the crucible while still soft, and when cold extracted with water; the clear solution, after separation of the cupric oxide, is then neutralised with nitric acid, and the potassium nitrate present separated, as far as possible, by crystallisation. The nitrite mixed with a little nitrate is obtained on evaporating the solution.

C. E. G.

Preparation of Anhydrous Sodium Sulphate from Glauber Salt. By A. R. Pechiney (*Chem. Centr.* [3], 1878, 816).—If Glauber salt solution is heated above 33° C. there separates gradually as much as 40 per cent. of the anhydrous salt. Balard has further shown that if to the solution of Glauber salt another soluble salt is added which contains the same metal or acid radicle, the salt is also separated. These facts are utilised as follows. The Glauber salt is dissolved by stirring it in water heated by steam to 40—50°, then magnesium sulphate or sodium chloride, or both, are added. When the salt has separated it is filtered off, or separated by a centrifugal machine. With 16 to 20 parts of sodium chloride and 100 of Glauber salt about 90 per cent. of the anhydrous salt is separated. With 45 parts of "salinen salt" (45 parts of sodium chloride mixed with 50 of magnesium sulphate) to 100 of Glauber salt, the whole of the anhydrous sodium sulphate is separated.

F. C.

Action of Chlorine on Strontia. By J. Konigel-Weisberg (*Deut. Chem. Ges. Ber.*, **12**, 511—513).—Chlorine has no action on dry strontium hydroxide, SrO_2H_2, but it converts the hydrates containing 5 and 8 molecules of water of crystallisation into strontium

chlorate and chloride. A small quantity of hypochlorite is also formed. W. C. W.

Ultramarine. By E. W. Buchner (*Deut. Chem. Ges. Ber.*, **12**, 234—235).—Ultramarine-blue can be prepared by heating a mixture of sodium, aluminium, and silicon, to a high temperature in a stream of sulphuretted hydrogen, washing the resulting black mass with water, and strongly igniting it in contact with air. The author asserts that metallic sulphides are not contained in ultramarine, for the above black mass, in which no blue can be discerned with a high power, gives blue particles visible to the naked eye when ignited either in air, in oxygen, or with potassium chlorate. Ch. B.

Amidonitrosulphide of Iron. By W. Demel (*Deut. Chem. Ges. Ber.*, **12**, 461—462).—The following method is found to be most fitted for the preparation of this body. 20 grams of potassium nitrite are dissolved in 300 c.c. of water, and heated to boiling; 40 c.c. of ordinary ammonium sulphide are added, and the mixture is heated for a short time. A solution of 33 grams of crystallised iron sulphate in 200 c.c. of water is gradually added, and the liquid boiled for ten minutes. On filtration, black crystals separate out, which decompose on exposure to air, but can be kept in a sealed tube containing carbonic anhydride. They are easily soluble in water, alcohol, and ether. When hydrochloric acid is added to the aqueous solution, sulphuretted hydrogen is evolved. Potash causes evolution of ammonia. When heated alone it glows, and is decomposed, leaving a residue of iron sulphide. The nitrogen of this compound is united to both the oxygen and hydrogen. The empirical formula is $FeSN_2H_2O_2$, which may be rationally expressed as $NH_2.S(NO_2)Fe : Fe(NO_2)S.NH_2$.

Attempts to prepare analogous bodies from nickel, cobalt, and manganese were unsuccessful. Somewhat similar bodies have been described before in *Annalen*, **107**, 120, and **125**, 302; and *Ber.*, **3**, 312. G. T. A.

Cobalt-Ammonium Compounds. By S. M. Jörgensen (*J. pr. Chem.* [2], **19**, 49—69).—In this communication the author describes the *bromopurpureo-salts* of cobalt; the series is in almost every respect analogous to that of the *chloropurpureo-salts* already described (this vol., 119). In both series the author regards two halogen (chlorine or bromine) atoms as more closely connected with the cobalt and ammonia present than the other atoms of the molecule. The leading facts adduced in proof of this view of the constitution of these compounds are: in double decompositions carried out in the cold, two halogen atoms remain associated with cobalt and ammonia; silver salts do not remove these halogen atoms. Concentrated sulphuric acid does not remove these two atoms, but only the remaining halogen atoms, as haloïd acid. In the formation of double salts, the halogen atoms "without the radicle" are alone replaced. The numbers attained by dividing sp. gr. by molecular weight (supposing the formulæ given to be molecular), are nearly identical when bromine is substituted for chlorine "within the radicle," but are very different when the substitution occurs "without the radicle," thus:—

$Cl_2.(Co_2 10NH_3).Cl_4$ molecular volume = 277·7 } Diff. = 3·9.
$Br_2.(Co_2 10NH_3).Cl_4$,, ,, = 281·6 }
$Cl_2.(Co_2 10NH_3).Cl_4$,, ,, = 277·7 } Diff. = 36·2.
$Cl_2.(Co_2 10NH_3).Br_4$,, ,, = 319·9 }

The starting point in the preparation of the bromopurpureo-salts is—

Bromopurpureocobalt Bromide, $Br_2.(Co_2 10NH_3).Br_4$.—This salt may be prepared by dissolving cobaltous carbonate in excess of hydrobromic acid, filtering from precipitated hydrate, and saturating the filtrate with ammonia, &c.; it is, however, more readily prepared by dissolving ordinary roseocobalt sulphate in hot water, with addition of a little hydrobromic acid, decomposing the solution by adding concentrated hydrobromic acid, and heating on a water-bath. The bromopurpureo bromide which separates out is washed with dilute hydrobromic acid (1 to 2), then with cold water, and finally with alcohol. Better still, the roseosulphate may be dissolved in ammonia, and then boiled with excess of hydrobromic acid. Bromopurpureocobalt bromide crystallises in blue-violet microscopic octahedrons, which exhibit dichroism; || axes showing violet and + axes yellowish-red. Crystallised from hot water acidified with hydrobromic acid, it appears as very dark, nearly black, octahedrons. Sp. gr. at 17·8 = 2·483 (water at 4° = 1). The salt is decomposed below a red heat, probably in accordance with the equation $Br_2.(Co_2 10NH_3).Br_4 = 2(4NH_3,CoBr_2) + N + NH_4Br + HBr + H$. 560 parts of water at 16° dissolve one part of this salt; it is insoluble in alcohol, ammonium or potassium bromide, and in aqueous hydrobromic acid. A concentrated solution may be prepared by treating the salt with cold dilute sulphuric acid, and subsequently with water. When shaken with freshly precipitated silver oxide and water, the bromopurpureo-bromide is decomposed with production of roseocobalt hydrate. On warming with silver nitrate, roseocobalt nitrate is produced.

Bromopurpureocobalt Chloride, $Br_2.(Co_2 10NH_3).Cl_4$, is prepared by heating the bromobromide with water at 40°, and allowing the solution so produced to drop into cold tolerably concentrated hydrochloric acid; the precipitate which forms is washed with dilute hydrochloric acid, and the acid is removed by washing with alcohol. The salt crystallises from hot water in dark-violet octahedrons, which exhibit optical properties similar to those of the crystals of the bromobromide. Sp. gr. at 16·8° = 2·095. The salt is slightly soluble in cold water; from this solution hydrobromic acid precipitates bromopurpureo-bromide.

Various qualitative reactions for the bromobromide and bromochloride are detailed.

Bromopurpureocobalt Mercuric Chloride, and *Bromide*,

$$Br_2.(Co_2 10NH_3).(Hg_3X_8)_2'' \text{ where } X = Cl \text{ or } Br.$$

Violet needles of the chloride are obtained on allowing a moderately warm solution of bromopurpureocobalt nitrate (see below) to flow into a cold concentrated solution of sodio-mercuric chloride; the crystals are quickly separated, washed with cold water, and dried over sulphuric acid. The bromide is precipitated in the form of brilliant lilac-

coloured crystals on adding potassio-mercuric bromide to a cold concentrated or moderately warm solution of bromopurpureobromide.

By mixing moderately warm solutions of bromopurpureobromide with varying quantities of sodio-mercuric chloride or mercuric chloride, a series of salts is obtained belonging to the bromopurpureo series, containing each six atoms of mercury, but varying amounts of chlorine and bromine. The most definitely marked of these salts are $Br_2.(Co_2 10NH_3).Hg_6Cl_{15}Br$, prepared by pouring bromobromide solution into excess of sodio-mercuric chloride, and

$$Br_2.(Co_2 10.NH_3).Hg_6Cl_{14}Br_2,$$

prepared by using an excess of mercuric chloride. The whole of the mercury is removed from these salts by agitating them with cold dilute hydrochloric acid, bromopurpureocobalt salt being produced.

Bromopurpureocobalt Platinic Chloride, and *Bromide*,

$$Br_2.(Co_2 10NH_3).(PtX_6)_2 \text{ where } X = Cl \text{ or } Br.$$

The chloride is obtained by adding hydroplatinic chloride to a cold concentrated solution of the bromochloride or bromonitrate; it forms greyish-brown microscopic crystals, insoluble in cold water. The bromide crystallises in red-brown brilliant forms, somewhat soluble in cold water, and is produced by adding sodio-platinic bromide to a cold concentrated solution of the bromobromide.

Bromopurpureocobalt Silicofluoride, $Br_2.(Co_2 10NH_3).(SiF_6)_2$.—This salt is prepared by dissolving the bromonitrate or chloride in water acidulated with sulphuric acid and warmed to about 35°, and pouring the solution into somewhat concentrated hydrofluosilicic acid. The salt crystallises in dark-violet rhombic tables, isomorphous with the chloropurpureo salt, and like it exhibiting dichroism. Cold water scarcely dissolves the crystals; they are insoluble in alcohol.

Bromopurpureocobalt Nitrate, $Br_2.(Co_2 10NH_3).(NO_3)_4$, is prepared in a manner similar to that employed in preparing the foregoing salt, only bromobromide is used in place of chloride or nitrate, and the solution is poured into nitric acid diluted with its own volume of water. The salt which separates in violet-coloured microscopic forms is washed with dilute nitric acid, and then with alcohol. It is less soluble in water than the bromochloride, but more soluble than the bromobromide. It may be crystallised from hot water acidulated with nitric acid, in dark-violet octahedrons, having sp. gr. of 1·956 at 17·1°. A solution of this salt is decomposed by addition of dilute hydrobromic acid with separation of bromobromide, and by dilute hydrochloric acid with formation of bromochloride.

Bromopurpureocobalt Sulphate, $Br_2.(Co_2 10NH_3).(SO_4)_2$, is most easily prepared by treating 1 mol. of the bromochloride with 12 to 14 mols. of cold concentrated sulphuric acid, diluting considerably with water after the escape of hydrochloric acid has ceased, and precipitating by addition of alcohol. If little water only be added, a blue-violet salt separates, which is most probably the acid sulphate. The normal sulphate may also be prepared, but by a more tedious process, from the bromobromide. It crystallises in small, very dark-violet octahedrons with brilliant lustre, which readily take up moisture and

pass into the hydrated sulphate, a salt which probably contains 6 mols. of water of crystallisation.

If the acid liquid, from which alcohol precipitates the normal sulphate be treated with a solution of iodine in potassium iodide, large, black, rectangular tables separate out, which polarise light very freely. This salt is probably *bromoperiodide.*

Bromopurpureocobalt Dithionate, $Br_2(Co_2 10NH_3).(S_2O_6)_2$, separates from the liquid produced by pouring a moderately warm solution of the bromochloride or bromonitrate into a cold concentrated solution of sodium thiosulphate. The crystals are four- or six-sided brilliant violet prisms, often more than a centimeter in length.

Bromopurpureocobalt Chromate, $Br_2.(Co_2 10NH_3).(CrO_4)_2$, is precipitated as a brown crystalline powder, insoluble in water, on adding potassium chromate to a cold concentrated solution of the bromobromide, or preferably bromochloride.

Bromopurpureocobalt Oxalate $Br_2.(Co_2 10NH_3)(C_2O_4)_2$, separates as long violet needles, when a solution of the bromochloride or bromonitrate in water at 30—40° is poured into a cold solution of ammonium oxalate. The crystals appear under the microscope as rectangular prisms, and exhibit dichroism. M. M. P. M.

Artificial Manganese Dioxide. By A. Görgeu (*Compt. rend.*, **88**, 796—798).—Crystals of manganese dioxide, resembling polianite in all their physical properties, namely, hardness, sp. gr., colour, and streak, are obtained by heating manganese nitrate gradually to 155—162°, and maintaining it at that temperature for 24 hours. When dried and titrated, it shows 36·5 to 36·75 per cent. oxygen. By oxidising protoxide and carbonate of manganese; by treating manganate and permanganate of potash with nitric acid; and by exposing manganic acid to spontaneous decomposition, only suboxides of manganese have been obtained, which do not alter by long exposure to air and distilled water.

By heating manganese nitrate in presence of the chloride and sulphate of manganese, or even with the nitrate of barium, calcium, magnesium, potassium, sodium, or iron, the purity of the resulting dioxide is not impaired.

The author considers these experiments to confirm the hypothesis of Deville and Debray (*ibid.*, **50**, 868) on the origin of native manganese dioxides. L. T. O'S.

On Tritungstates. By J. Lefort (*Compt. rend.*, **88**, 798—801). A description of the mono- and di-tungstates has already appeared (*ibid.*, **87**, 748, and this vol., p. 355). The tritungstates are prepared by decomposing sodium tritungstate with metallic acetates, and mixing the solutions with alcohol, when gummy precipitates are formed, which are washed with alcohol and dried at 100°. With the exception of the tritungstates of lead, barium, and strontium, they are soluble in water. In the viscous or dry state, the tritungstates are stable bodies, but when treated with water they decompose into ditungstates and metatungstates. When treated with acids, the tritungstates are decomposed with liberation of tritungstic acid, which in its turn is

decomposed, and tungstic acid deposited. The general formula for the tritungstates of the dyad metals is $(WO_3)_3M''O + x$ Aq.; the mercury compound, however, obtained by adding mercuric acetate to sodium tritungstate has the composition—

$$5(WO_3).HgO = 3(WO_3).HgO.2(WO_3),$$

affording a further proof of the existence of pentatungstates.

The tungstates of the sesquioxides form a group of salts represented by the following formulæ:—

Mono tungstates		$(WO_3)_2M_2O_3$
Di ,,		$(WO_3)_3M_2O_3.WO_3$
Tri ,,		$(WO_3)_3M_2O_3.2(WO_3)$
Tetra ,,		$(WO_3)_3M_2O_3.3(WO_3)$

It is thus seen that the acid tungstates are formed from the neutral salt by its union with one, two, or three molecules of the acid radicle, thus forming di-, tri-, and tetra-tungstates respectively, and not as might have been expected by its union with two, three, or four times the number of acid radicles which it itself contains.

The author appends a table of the tritungstates of the monoxides and sesquioxides obtained. L. T. O'S.

Scandium. By L. F. Nilson (*Deut. Chem. Ges. Ber.*, **12**, 554—557).—In preparing ytterbia by Marignac's method, which depends on the difference in the action of heat on the nitrates of erbium and ytterbium, the author observed that the oxide obtained from the insoluble basic nitrate had the molecular weight of 127·6, and exhibited characteristic absorption lines in the orange, yellow, green, and blue parts of the spectrum, totally distinct from those produced by erbia.

Scandium forms a white oxide, probably ScO_2, which dissolves slowly in nitric acid. Oxalic acid completely precipitates the scandium from this solution. The nitrate decomposes at a lower temperature than ytterbium nitrate. W. C. W.

Ytterbia. By L. F. Nilson (*Deut. Chem. Ges. Ber.*, **12**, 550—553).—The author has continued Marignac's research on erbia, and confirms the conclusions arrived at by that chemist, viz., that the substance known as erbia is a mixture of two oxides: one of these which he calls *erbia* is rose-coloured, and exhibits characteristic absorption spectra, whilst the other, *ytterbia*, is colourless, and does not produce absorption bands in the spectrum.

The molecular weight of YbO is 131·92—132·17. W. C. W.

Chlorostannates of the Rare Earths. By P. T. Cleve (*Bull. Soc. Chim.* [2], **31**, 195—197).—By mixing concentrated solutions of tin tetrachloride and of lanthanum, yttrium, cerium, and didymium chlorides, and evaporating slowly over caustic potash, the author has obtained chlorostannates of these metals in long, bulky, very deliquescent crystals. The formulæ deduced from the analyses are: lanthanum salt, $2La_2Cl_6.5SnCl_4.45H_2O$ (similar to yttrium chloroplatinate,

$2Y_2Cl_6.5PtCl_4.51H_2O$); cerium salt, $Ce_2Cl_6.2SnCl_4.18H_2O$; didymium salt (forms large red crystals) $Di_2Cl_6.2SnCl_4.21H_2O$; yttrium salt, $Y_2Cl_6.2SnCl_4.16H_2O$.

The author confirms Marignac's conclusions with regard to *terbia*, the third earth of gadolinite: he has also succeeded in extracting from gadolinite a small quantity of Marignac's alleged new earth *ytterbia*. In order to test Delafontaine's suggestion that didymium oxide is a mixture, he prepared pure samples of this earth from cerite, gadolinite, and orthite, but could discover no appreciable difference in the absorption spectra of the three solutions. J. M. H. M.

Purification of Mercury. By L. Meyer (*Deut. Chem. Ges. Ber.*, **12**, 437—439).—The method proposed by the author is to allow the mercury to fall in a fine stream through a solution of ferric chloride. The ferric chloride is contained in a long tube dipping into a cylinder containing mercury, and provided with a side tube through which the purified mercury flows off. P. P. B.

Purification of Mercury. By J. W. Brühl (*Deut. Chem. Ges. Ber.*, **12**, 576—577).—The apparatus described by Victor Meyer (*Ber.*, **12**, 437) for purifying mercury by means of a solution of ferric chloride, cannot in the opinion of the author be used with advantage when chromic acid is employed as the oxidising agent. W. C. W.

Mercuric Iodide. By H. Köhler (*Deut. Chem. Ges. Ber.*, **12**, 608—609).—Mercuric iodide melts at 253—254°, forming a blood-red liquid, and not at 238° as stated in Gmelin-Kraut. It can be obtained in large red crystals by recrystallisation from hot concentrated hydrochloric acid. W. C. W.

Note.—Carnelley and Williams found that mercuric iodide, prepared by triturating mercury and iodine in presence of a small quantity of alcohol, melts at 241° (corr.).—W. C. W.

Mineralogical Chemistry.

Application of the Author's Atomic Theory to certain Minerals. By M. A. Gaudin (*Compt. rend.*, **88**, 158—161).—This paper relates to a theory by which the author seeks to deduce the forms and angles of crystals from configurations of their constituent atoms. The minerals referred to are harmotome, albite, and tourmaline. R. R.

Constitution of Coal. By E. Guignet (*Compt. rend.*, **88**, 590—592).—Many chemists have succeeded in dissolving out small quantities of bituminous matter from coal by means of ether, benzene, carbon bisulphide, and chloroform. The author has obtained better results with phenol.

The coal, dried at 110°, and reduced to the finest possible state of subdivision by grinding with water until it assumes a clear brown colour and is quite soft to the touch, yields as much as 4 per cent. of its weight to dry boiling phenol. The filtrate is brown, and on the addition of alcohol deposits the dissolved matter in brown flocks, which are thrown on a filter and washed with alcohol until free from phenol. Nitric acid attacks this substance with some difficulty, forming a yellow product. On repeatedly treating the original coal with nitric acid, filtering, evaporating the filtrate to dryness, taking up with water, boiling with barium carbonate, filtering, and precipitating the barium in the filtrate by sulphuric acid, a solution is obtained containing *trinitroresorcinol* (oxypicric acid). The barium carbonate precipitate contains barium *oxalate*, besides barium sulphate and ferric hydrate. The coal residue insoluble in nitric acid contains nitro-products similar to the nitro-celluloses, and on heating decomposes with explosion or evolution of red fumes; it also contains products giving a brown solution with sodium hydrate and even with ammonia.

The original coal, evaporated to dryness with strong caustic soda, and distilled at 400° in an iron retort, yields a clear yellowish liquid containing amongst other things ammonia and aniline, but no *resorcinol*. The distillation residue treated with water gives a deep brown solution, which, neutralised with an acid, deposits a large quantity of brown substance resembling the ill-defined compounds confounded under the names *ulmin*, *humic acid*, &c. By treating the coal with concentrated or fuming sulphuric acid, or nitro-sulphuric acid, similar products are obtained, in the latter case mixed with nitro-products.

J. M. H. M.

Bernadinite, a Resinous Mineral from California. By J. M. Stillman (*Deut. Chem. Ges. Ber.*, **12**, 567—570).—Bernadinite is a yellowish-white, porous, friable substance. It floats on water, but when the air contained in its pores is expelled, its sp. gr. is 1·166. This mineral softens at 100°, but does not melt at 140°. It is partly soluble in alcohol, ether, and carbon bisulphide, it also dissolves in soda, but is reprecipitated from the alkaline solution by acids. An analysis of the mineral gave the following results:—

H_2O, 3·87; C, 64·46; H (not as H_2O), 8·75; O (not as H_2O), 22·80; Ash, 00·12 per cent.

W. C. W.

Composition of the Combustible Gases in the Stassfurt Potash Mines. By H. Precht (*Deut. Chem. Ges. Ber.*, **12**, 557—561).—The gas which issues from the salt beds of Stassfurt has the following composition by volume:—H, 93·05; CH_4, 0·778; N, 5·804; CO_2, 0·180; O, 0·185, and CO a trace. The gas is inodorous and has a density of 0·121 compared with air.

The gas which is liberated on dissolving the abraum salt in water has a disagreeable smell. It contains CO_2 25·7 per cent., H, 3·8; and hydrocarbons 2·5 per cent.

W. C. W.

Diaspore from Jordansmühl. By P. Klein (*Jahrb. f. Min.*, 1878, 749—750).—This mineral was hitherto not known to occur in Germany. It was found on some serpentine rock from the above

locality which had been used for repairing roads. The diaspore of Jordansmühl is perfectly colourless and massive, occurring in laminated particles several centimeters in size, but no crystals were found. It gave all the characteristic blowpipe reactions of diaspore, and its optical properties were those of a rhombic mineral. No iron was present in it. The outward appearance of this mineral is nearly that of the diaspore from Texas, Pennsylvania, but their modes of occurrence are dissimilar, the American mineral being accompanied by chlorite and granular chromite, whilst that from Germany is enclosed in a massive garnet-rock (whose clefts contain numerous small, colourless, or smoky garnets) which constitutes a layer in a serpentine-mound near Jordansmühl. C. A. B.

The Hydrohæmatite of Neuenburg. By M. Bauer (*Jahrb. f. Min.*, 1878, 747).—This mineral occurs in large quantity in the brown-iron ore veins, at Neuenburg. It resembles brown-iron ore very closely, but can be distinguished by its dark blood-red streak from the latter mineral, which has a yellow streak; also by fractured surfaces exhibiting a dark greyish-black colour with a reddish tinge, somewhat like the colour of some massive cuprite specimens. The hydrohæmatite of the above locality occurs as a botryoïdal crust, resting upon the brown-iron ore, and constitutes about $\frac{1}{5}$th of all the ore obtained in that district. C. A. B.

Phosgenite from Monte Poni, Sardinia. By V. Hansel (*Jahrb. f. Min.*, 1874, 754).—Phosgenite was first discovered in the lead mines of Monte Poni by Sella (*Jahrb. f. Min.*, 1874, 839). The crystals of this locality are remarkable for their size and beauty. The author examined a crystal which was attached to granular galena, and had a diameter of from 8 to 9 mm., and a length of 2 cm. It exhibited the following forms in combination; viz.: ∞P .∞P2. 0P. 2P2. 2P∞. ∞P∞. The faces of ∞P were vertically striated. The calculated values correspond to the axial relationship given by von Kokscharow; viz.: $a : c = 1 : 1{\cdot}08758$ from his examination of the phosgenite crystals of Gibbas, whence it follows that the Monte Poni and Gibbas phosgenites are identical. C. A. B.

Pelagosite. By G. Tschermak (*Jahrb. f. Min.*, 1878, 751).—The author examined numerous specimens of limestone and dolomite from the Mediterranean coast, which were covered with a grey, shining, varnish-like substance. This substance forms where the waves act upon the rock. No organised structure was observed, but a chemical examination proved it to consist mostly of calcium carbonate. The finest specimens of this substance came from the island of Pelagosa, in the Adriatic, from whence it derived its name. Descloiseaux and Vélain observed this peculiar incrustation on felspathic rocks in Corsica, on the coast of Oran, and on the basaltic lavas on the coast of Réunion. C. A. B.

Ankerite, from Phœnixville. By G. Koenig (*Jahrb. f. Min.*, 1878, 747).—The ankerite of this locality occurs in well-developed,

brown rhombohedrons, which do not exhibit the slightest trace of rounding off. These crystals are attached to colourless, crystalline ankerite, which has a strong vitreous lustre. Terminal edge-angle of R = 105° 59′. Sp. gr. = 2·953. Chemical composition as follows, viz. :—

CO_2.	CaO.	FeO.	MgO.	
44·56	28·60	14·41	13·03	= 100·00

The formula deduced from the above is $Mg_3Fe_2Ca_5C_{10}O_{30}$.

C. A. B.

Manganosite from Langban, Sweden. By P. Klein (*Jahrb. f. Min.*, 1878, 750—751).—Manganosite was discovered by Blomstrand, at Lund in Sweden, and described by him as occurring in calcite in dark, irregular grains (exhibiting a distinct cubical cleavage), and having a dark emerald-green colour by reflected light, and a ruby-red shimmer in transmitted light. The author found it to be isotropic, consequently regular, and its colour was dark emerald-green both in reflected and transmitted light. The mineral becomes coated with a film of brown oxide on exposure to the air for a few weeks, and no doubt it was this occurrence which caused Blomstrand to suppose that it exhibited a ruby-red colour in transmitted light. The embedded grains, 1 cm. in diameter, are built up of minute laminated octahedrons, which are always coated with a thin film of oxide. C. A. B.

Optical Properties and Crystalline Form of Tridymite. By A. v. Lasaulx (*Jahrb. f. Min.*, 1878, 752—753).—Schuster concluded from his examination of tridymite (*Jahrb. f. Min.*, 1878, 533) that it crystallised in the *asymmetrical* system, and von Lasaulx confirms this opinion, although he had previously stated that tridymite was a *rhombic* mineral (*Jahrb. f. Min.*, 1878, 408). The author lately examined numerous specimens from Tardone Mountain in Ireland, Perlenhardt in the Siebengebirge, San Cristobal in Mexico, Mont Dore, &c., &c., and arrived at the following conclusions, viz.: (1.) Tridymite is an asymmetrical mineral, although its forms approach very closely those of the rhombic system. (2.) The apparently hexagonal plates are twins, analogous to those of monosymmetrical mica, or to those of a rhombic mineral of the aragonite group. The twin-plane is a face of the prism, but there is also another twin-law, which was first discovered by vom Rath, viz.: "the twin-plane a face of a pyramid out of the zone of the prism-edge." C. A. B.

Occurrence of Thomsonite at Läven. By W. C. Brögger (*Jahrb. f. Min.*, 1878, 753—754).—The author discovered crystals of thomsonite, 2 mm. long, ½ mm. wide, and ¼ mm. thick, clothing small cracks and hollow spaces in a specimen of decomposed eläolite. The faces in the prismatic zone were striated, the macropinacoid often predominated. The terminals of the crystals were either the well-known obtuse dome of thomsonite, $x\breve{P}\infty$, occurring alone, or else an acuter brachydome with a macrodome. The axial relationship was found to be $a : b : c = 0{\cdot}9925 : 1 : 1{\cdot}0095$, and the form observed, ∞P. $\infty P\bar{\infty}$. $\infty\breve{P}\infty$. $\frac{1}{2}\breve{P}\infty$. $\frac{1}{4\,5}\breve{P}\infty$. $P\bar{\infty}$. C. A. B.

Simultaneous Occurrence of Grossular, Zoisite, Stillbite, and Leidyite, a New Species. By G. Koenig (*Jahrb. f. Min.*, 1878, 751—752).—The above-mentioned minerals are found at Leiperville, on the Crum Creek, near Chester, Delaware Co., in the crystalline slates which predominate there.

Grossular occurs in fine crystals 2 cm. in size, and exhibiting the combination $\infty O.2O2$, also in grains. H. = 6. Sp. gr. = 3·637. Vitreous lustre with a resinous lustre on fractured surfaces. Brownish to amber-yellow in colour. Only attacked by hydrochloric acid after ignition. A light grass-green to whitish-green, perfectly transparent, granular variety of grossular is also found occasionally. Strong manganese reaction.

Zoisite.—Massive, or else in aggregates of prismatic crystals. H. = 6. Sp. gr. = 3·642. Light rose-red. Not attacked by hydrochloric acid. Fuses to a white enamel with intumescence before the blow-pipe in the oxygen flame.

Stillbite occurs in the usual crystal forms, having, however, a peculiar olive-green colour, in hollows in garnets and zoisite.

Leidyite occurs stalactitic (botryoidal or in nodules) on quartz, but more particularly in hollow spaces in garnet and zoisite. H. = 1. Grass- to olive-green or greenish-grey colour. Streak white. Resinous lustre. Fuses before the blow-pipe to a yellowish-green glass, evolves water on being heated in a matrass, and is easily soluble in hydrochloric acid. Its chemical composition was found to be as follows, viz. :—

SiO_2.	Al_2O_3.	CaO.	MgO.	FeO.	H_2O.	
15·40	16·82	3·15	3·07	8·50	17·08	= 64·02*

from which the formula $\overset{II}{R}_2Si_5O_{15} + 5H_2O$ is deduced. Koenig concludes that leidyite (named in honour of Joseph Leidy, of Philadelphia) is a zeolitic mineral, and like the stillbite, a secondary product of the decomposition of the grossular or zoisite. C. A. B.

Chemical Composition of Nepheline, Cancrinite, and Microsommite. By H. Rauff (*Jahrb. f. Min.*, 1878, 745—747).—*Nepheline.*—The author wished to ascertain whether this mineral was a pure semi-silicate, or a mixture of normal silicates with semi-silicates. Analysis made of very pure material furnished the following results, viz. :—

	SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O	K_2O.	
No. I..	43·91	33·56	1·58	0·23	15·58	4·93 =	99·79
„ II..	44·41	33·47	1·76	0·14	16·19	4·54 =	100·51
„ III..	43·79	32·80	1·32	0·20	16·23	4·82 =	99·16

The author found also 0·12 and 0·14 per cent. of water, which he says may be considered basic. From the above results the formula $\overset{I}{R}_8Al_4Si_9O_{34}$ is obtained, and nepheline must be considered to be a combination of normal silicates with semi-silicates.

Cancrinite.—This mineral has lately been doubted as an independent

* There is some error in these numbers, probably in the amount of lime; in the *Jahrbuch*, from which they are taken, the total is given as = 100·03.—H.W.

species, but the author concludes from his chemical and microscopical examinations that it is a homogeneous mineral having the sp. gr. 2·450, and the following composition, viz. :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	CO_2.	H_2O.
No. I.	37·40	28·08	0·37	7·09	17·96	0·16	6·20	3·99=101·25
„ II.	37·16	28·32	0·51	6·82	17·54	0·23	6·12	4·07=100·77

The formula corresponding with the above is $Na_8\overline{Al}_4Si_9O_{34} + 2CaCO_3 + 3H_2O$.

Microsommite.—This remarkable sublimation-product of the Vesuvian lavas becomes the more interesting on account of the discovery in it by the author of carbonic acid. An analysis of a perfectly colourless, pure crystal (sp. gr. 2·44) gave the following results, viz. :—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Cl.	SO_3.	CO_2.
31·94	28·18	10·23	11·85	7·84	7·04	3·69	1·47=102·24

Deducting 1·59 per cent. of oxygen equivalent to 7·04 per cent. of chlorine, the total = 100·65. Rauff believes that a small quantity of silica is replaced by carbonic acid. The formula he assigns to the mineral is $\left\{\begin{matrix}CaSO_4\\4.NaCl\end{matrix}\right\} + 6(\overset{I}{R}_2\overline{Al}Si_2O_8)$.

Microsommite and nepheline are almost identical in their crystallographical characteristics, the crystal of microsommite analysed exhibiting the following combinations, viz.: $\infty P.\ \infty P2.\ \infty P\frac{3}{2}.0P.\frac{1}{2}P$, whilst the axial relations and interfacial angles of the two minerals are as follows, viz. :—

	Microsommite.	Nepheline.
$a : c$ =	1 : 0·836686	1 : 0·8390
Terminal edge of P.... =	139° 20′	139° 17′
Lateral edge of P..... =	88 1	88 10
Terminal edge of $\frac{1}{2}P$.. =	154 52	154 49
Lateral edge of $\frac{1}{2}P$ =	51 34	51 41

C. A. B.

The Nepheline Rock of Meiches in the Odenwald. By v. Klipstein (*Jahrb. f. Min.*, 1878, 722—725).—The author first described this rock in 1840 (Nephelinfels von Meiches: *Karsten and von Dechen's Archiv. f. Min., &c.*, **14**, 248), and visited the locality again in 1878, when he observed for the first time that the nepheline rock was in contact with basalt, and often so intimately intergrown with it that it almost appeared as though the one rock passed over into the other. Zirkel gave a more detailed description of the above-mentioned rock (*Untersuchungen über die mikroskopische Zusammensetzung und Structur der Basalt-Gesteine*), but was unable to compare it with allied rocks, on account of the small quantity of material at his disposal. According to Zirkel, felspar occurs very seldom and in very small quantity in the typical nepheline basalt of the Löbanerberg and Katzenbuckel; it is therefore a striking characteristic of the rock from Meiches, that it occurs as sanidine, evenly distributed throughout the rock either crystalline or in distinct well-developed individuals, in drusy spaces. A macroscopical examination showed that the nepheline and augite individuals in the nepheline-rock of Meiches have a radia-fibrous structure

and are intimately intergrown. Sometimes large nepheline crystals inclose smaller crystals of the same mineral and also augite crystals. Apatite needles were also occasionally observed, but the author was unable to detect the presence of leucite or melilite (stated to be present by other investigators), although he examined a great number of specimens. Titanite was also found to be extremely rare in this rock. Von Klipstein suggests that it would be extremely interesting to obtain answers to the following questions, viz.: (1.) Does any metamorphosis of the constituents of the nepheline rock occur in its passage over to the microcrystalline rock (basalt)? (2.) Does the basalt contain the same relative amounts of felspar as the nepheline-rock? (3.) Do the volcanic glasses and other amorphous substances present in many basalts, replace the felspar, and if so, can their presence be a proof that microcrystalline felspar is more fusible than the other constituents? C. A. B.

Occurrence of Tin in Silicates. By F. Sandberger (*Jahrb. Min.*, 1878, 748—749).—It was proved by Killing (*Jahrb. f. Min.* 1878, 657) that the mica of the Schwartzwald gneiss contains all the metals found in the veins of Schapbach, with the exception of silver. Tin was not found in the *dark-coloured* micas, from which it was concluded that this metal occurred only in a certain class of micas. As granite containing lepidolite and some other minerals also incloses tinstone either disseminated or in veins, Sandberger submitted the lepidolite of Paris in Maine (U.S.A.) and Rozena in Moravia (where hitherto the presence of tin had not been suspected) to a careful chemical analysis, and found a considerable amount of tin in each, the Paris lepidolite containing the most. A careful macroscopical examination of the lepidolite laminæ has failed to detect the slightest trace of tin-stone grains. It is strange that all previous analysts of these minerals had ignored the presence of metals which are precipitated by sulphuretted hydrogen. The author thinks it highly probable that these micas are the original matrix of tin-stone, which was deposited in them from complicated compounds by chemical and aqueous action. The stannic oxide partially replaces the silica in these micas, just as the isomorphous titanic acid has often been found to do in other micas, and from this discovery, the author considers it probable that a silica crystallising in the quadratic system will be discovered sometime. The lepidolite of Penig in Saxony and Utoen in Sweden has also been found to contain tin-stone. C. A. B.

The Crystal System of Mosandrite. By W. C. Brögger (*Jahrb. f. Min.*, 1878, 753).—The author examined some well-defined crystals of mosandrite found in the Island of Läven, and enclosed in leucophane. The crystal system was found to be monosymmetrical, the axial relations being $a : b : c = 1{\cdot}0811 : 1 : 0{\cdot}8135$; $\beta = 71° 24\frac{1}{2}'$. The crystals are "long-prismatic" and exhibit the following forms, viz.: ∞P . $\infty P2$. $\infty P\infty$. $\infty P\infty$. — P. — $P\infty$. Cleavage orthodiagonal. Strongly pleochromatic. One twin-crystal was observed, the twin-plane being the orthopinacoid. The mosandrite which occurs imbedded in

felspar is characterised by a combination of several prisms, which do not occur on the mosandrite imbedded in leucophane. C. A. B.

The Leucitophyr of Lake Averno. By E. Kalkowsky (*Jahrb. f. Min.*, 1878, 727—729).—F. Hoffmann stated (*Karsten's Archiv.*, **13**, 222) that banks of a leucite rock occurred alternating with banks of a pumice-conglomerate on the Lago d'Averno, but vom Rath and Guiscardi visited the locality and were unable to discover any leucite rock, and doubted Hoffmann's statement. (*Zeitsch. d. Deutschen Geol. Ges.*, **18**, 1866.) Vom Rath visited the same spot again in 1877, with a similar result (*Abh. d. k. Akad. Wissench.*, Berlin, 1877). Kalkowsky was more fortunate and re-discovered the leucite rock by going from Pozzuoli, leaving the shore of the lake near Monte Nuovo, and walking to the north of the mountain (between it and Monte Barbaro) until the lake came again into sight behind the Maglioni estate. On following the road a short distance, he observed before him two distinct layers or banks of leucitophyr, which were, however, much disintegrated by atmospheric action. The leucitophyr-bank of Tenuta Maglioni is from 20 to 30 cm. in thickness, and enclosed at a distance of 15 meters and 2 meters above the level of the road. The leucitophyr-bank near Cuma has similar dimensions. The rock is slightly porous, of a grey colour, fine-grained, and contains numerous leucite individuals, porphyritically disseminated throughout the mass, and which vary from 1 to 2 mm. in diameter. Augite was observed occasionally, but the author did not discover the presence of olivine. The microscopical characteristics of the Lago d'Averno leucites are identical with those exhibited by Vesuvian leucite, as they consist of two-thirds leucite and one-third plagioclase. Orthoclase was not present. Apatite occurred but very sparingly, and the magnetite observed was partially surrounded by reddish-yellow ferric oxide, thus proving the rock to be undergoing a slow decomposition. C. A. B.

Metallic Granules of Sporadosidereal Meteorites. By S. Meunier (*Compt. rend.*, **88**, 794—796).—Since the metallic granules in sporadosidereal meteorites are not spherical, but angular and ramified, the author concludes that the metals have been reduced at a temperature below their melting points. He also supposes the meteorites to be formed in very low strata, where the metals are reduced by the action of heat in presence of lignite. L. T. O'S.

The Meteorite of Ysadâny, Temesvar. By E. Cohen (*Jahrb. f. Min.*, 1878, 747—748).—This meteorite fell on the 31st of March, 1875. The outer surface is brownish-black in colour, and a macroscopical examination shows that it consists of a fine-crystalline, light-grey ground-mass, which encloses grains of the colour of magnetite, grains or laminæ of nickeliferous iron, and numerous crystalline grey globules, which exhibit a rough outer surface; thin sections were prepared with great difficulty. The globules were of two kinds mineralogically, one kind consisting of narrow rhombic prisms, which exhibited the characteristics of enstatite, the other kind consisting of colourless aggregations of olivine grains. There was also evidence of

the presence of a third mineral as an accessory, most probably hypersthene. The metallic minerals (troilite and nickeliferous iron) were imbedded in the "ground-mass," and between them was a clouded semi-translucent substance, which had apparently the same composition as the globules. The author classes the meteorite of Ysadány with those of the chondrite type, as it is identical with the Lancé, Gopalpar, and Pultusk meteorites. C. A. B.

A Meteorite belonging to the Eukrite Group. By — Daubrée (*Compt. rend.*, **88**, 544—547).—On the 14th July, 1845, at three o'clock in the afternoon, an incandescent stone fell in the Commune du Teilleul (Manche). Its shape was roughly that of a very flat pentagonal prism, with blunted edges, and its weight 780 grams. It was completely covered with a blackish crust, which, contrary to the usual rule, presented a brilliant surface, intersected by a network of veins, showing that the fused matter was disturbed at the moment of solidification. The crust viewed in thin scales is vitreous, transparent, and greenish. The body of the meteorite presents dark-green and white grains, in a light-green mass. The mineral substances observed to be present are triclinic feldspar, anorthite, enstatite, diallage, peridote, nickeliferous iron, pyrrhotine, and chrome iron. The meteorite contained no substances soluble in water, and the 26·3 per cent. of it soluble in nitric acid had the following percentage composition:— Silica, 39·20; alumina, with a little oxide of iron, 44·56; magnesia, 1·40; lime, 14·70. The external characters of the meteorite would place it among those to which Rose has given the name of *howardite*, but its chemical composition makes it a member of the same author's group of *eukrites*. Similar rocks are found among the lavas of Ireland. R. R.

Organic Chemistry.

Specific Gravity Determinations of Solid Organic Compounds. By H. Schröder (*Deut. Chem. Ges. Ber.*, **12**, 561—567).

	Sp. gr.	Sp. vol.
Pure cane sugar (crystal)	1·588	215·4
„ (powder)	1·588	215·4
Milk sugar	1·525	236·1
Mannitol	1·489	122·2
Erythrol	1·452—1·449	84—82
Carbamide	1·333	45·0
Sulphocarbamide	1·406	54·1
Oxamide	1·667	52·8
Acetamide	1·159	50·9
Propionamide	1·037	70·4
Chloral hydrate	1·818	91·0
Butyl-chloral hydrate	1·695	114·2

	Sp. gr.	Sp. vol.
Tetramethylammonium iodide	1·844	109·1
Tetrethylammonium iodide	1·559	164·6
Benzoic acid	1·297	94·7
Quinol (hydroquinone)	1·328	82·6
Pyrocatechol	1·348	81·6
Resorcinol	1·289	85·3
Pyrogallol	1·463	86·1
Orthonitrophenol	1·451	95·8
Paranitrophenol	1·469	94·5
Trinitrophenol	1·777	129·0
Paradichlorobenzene	1·467	100·2
Paradibromobenzene	2·222	206·2
Paranitraniline	1·433	96·3
Metanitraniline	1·430	96·5
Azobenzene	1·223	148·8
Diphenylamine	1·161	145·6
Potassium isocyanate	2·056	39·4
Mercury methyl chloride	4·063	61·7
Mercury ethyl chloride	3·503	75·5
Mercurydiphenyl	2·340	151·3
Mercurydinaphthyl	1·944	233·6
Phenylphosphinic acid	1·475	107·1
Phenylarsinic acid	1·760	114·8
Diphenylphosphinic acid	1·331	163·8
Diphenylarsinic acid	1·545	169·6
Naphthylphosphinic acid	1·435	145·0
Naphthylphosphorous acid	1·377	139·5
Calcium oxalate, $CaC_2O_4H_2O$	2·200	65·0
Barium benzoate, $Ba(C_7H_5O_2)_2 3H_2O$	1·808	239·6
Barium acetate (dried at 130°)	2·440	104·5
Silver cinnamate	2·073	123·1

From a comparison of the preceding data, it will be seen that as a rule, each atom of carbon, hydrogen, oxygen, and nitrogen occupies one stere.

The following compounds are isosteric: oxamide, $C_2O_2N_2H_4$, and sulphocarbamide, CSN_2H_4, sp. vol. 53.

Benzoic acid, $C_7H_6O_2$, and paranitrophenol, $C_6H_5NO_2O$, sp. vol. 94·6. Paranitraniline, $C_6H_4NH_2NO_2$, and orthonitrophenol, $C_6H_5NO_2O$, sp. vol. 96. The specific volumes of the chlorbenzenes increase by two steres $= 2 \times \overline{5{\cdot}91}$ for each atom of hydrogen which is replaced by chlorine, *e.g.*, $C_6H_3Cl_3$, $19 \times \overline{5{\cdot}91} = 112{\cdot}29$, $C_6H_2Cl_4 = 21 \times \overline{5{\cdot}91} = 124{\cdot}11$, $C_6HCl_5 = 23 \times \overline{5{\cdot}91} = 135{\cdot}93$ observed. W. C. W.

Organic Ferricyanogen Compounds. By O. Bernheimer (*Deut. Chem. Ges. Ber.*, **12**, 408—410).—*Tetramethylammonium ferricyanide* $(NMe_4)_6Fe_2Cy_{12} + 6H_2O$, is prepared by acting on silver ferricyanide with a cold saturated solution of tetramethylammonium iodide, and concentrating the solution filtered from the silver iodide in a vacuum over

sulphuric acid. It forms small plates or quadratic prisms, which are easily soluble in water and hot alcohol, but insoluble in cold alcohol and ether. It is hygroscopic, and is easily decomposed by heat, yielding vapours having the characteristic odour of methylamine. Ferric chloride produces a reddish-brown coloration in its aqueous solutions; ferrous sulphate produces a blue precipitate; sulphuric acid liberates hydroferricyanic acid from the concentrated solutions of this salt.

The tetrethylammonium ferricyanide is prepared in the same manner as the above, which it resembles in its properties; it crystallises with 8 mols. of water. P. P. B.

Presence of Nitrils in the Distillate obtained by the Calcination of Residues from Beet-root Molasses. By C. Vincent (*Bull. Soc. Chim.* [2], **31**, 156—157).—Impure methyl alcohol holding in solution various nitrils constitutes the principal product obtained by the destructive distillation of the "vinasses," or residues from the fermentation of beet-root molasses. After neutralisation and rectification, this distillate was boiled with milk of lime for 30 hours, or as long as ammonia was evolved, in order to decompose the nitrils, and to obtain from them the corresponding acids; the latter having been converted into soda salts, were crystallised and the sodium acetate, which was most abundant, separated as far as possible. The mother-liquors were treated with alcohol and sulphuric acid to etherify the acids, and the compound ethers were separated by fractional distillation; from these the acids were recovered by saponification. In this manner, propionic acid boiling at 141·6°, butyric acid boiling at 163—164°, and valeric acid at about 175° were isolated, thereby proving the existence in the original distillate of the cyanides of ethyl, normal propyl, and isobutyl. J. W.

Products of Distillation of Alcohol. By I. Pierre and E. Puchot (*Compt. rend.*, **88**, 787—790).—In the rectification of commercial alcohol, the liquid at a certain stage of the distillation assumes a colour varying from a sage-green to an intense yellow; this liquid in contact with the skin produces a stain similar to that of iodine. There also distils over a liquid having a strong smell of pepper, and at the end of all the distillations there remains in the retort an oily residue floating on the water, which sometimes resembles tar in appearance, and which distils between 200° and 330°. The authors having reproduced these phenomena synthetically, find they are produced by the action of dilute alkaline solutions on the aldehyde present, which causes certain modifications and condensation-products of the aldehyde, resulting finally in the formation of aldehyde-resin which distils between 200° and 330°. L. T. O'S.

Diallylisopropyl Carbinol. By Riobinine and A. Saytzeff (*Bull. Soc. Chim.* [2], **31**, 199).—The synthesis of this body is interesting because its empirical formula is the same as that of borneol, and by subtraction of the elements of water we get the formula of a hydro-

carbon, $C_{10}H_{16}$, containing isopropyl, a radicle believed to exist in the terpenes.

Diallylisopropyl carbinol is prepared by the action of allyl iodide on isobutyl ether, the process being similar in all respects to that for the preparation of diallylmethyl carbinol. It is a colourless liquid (b. p. 182—185°), of pungent characteristic odour. Its density at 0° is 0·8512. It appears to oxidise slowly by contact with the air, giving rise to the formation of carbonic and acetic acids. J. M. H. M.

An Amyloïd Substance Peculiar to the "Asques" of Pyrenomycetes. By L. Crié (*Compt. rend.*, **88**, 759—760).—In the *Sphœria Desmazierei* (Berk), at a certain age, there appears at the top of the "asque" a globule, which increases in size and grows by introsusception.

It gives a blue colour with iodine. Its chief characteristics are (1) its formation in darkness by a protoplasm destitute of chlorophyll, and (2) its insolubility in the cellular fluid. The author proposes the name *amylomycin* for this new amyloïd matter. L. T. O'S.

Composition of Wood. By J. Thomsen (*J. pr. Chem.* [2], **19**, 146—168).—The action of cold dilute caustic alkali on the wood of trees of the birch class results in the withdrawal of a substance which is isomeric with cellulose, $C_6H_{10}O_5$, and to which the author gives the provisional name of "wood gum" (*Holzgummi*). This substance is identical with the "Pectin substance" of Poumarède and Figuier (*J. pr. Chem.*, 1847, **42**, 25). Wood gum is most easily prepared from beech sawdust, by digesting with ammonia solution, washing, again digesting with caustic soda, filtering, precipitating the filtrate with alcohol, washing with alcohol, digesting with a little dilute hydrochloric acid to remove mineral matter, repeatedly washing with alcohol, and finally with ether.

As thus prepared, wood gum is a colourless powder, insoluble in cold water, but soluble in about 50 parts of boiling water, forming a liquid which becomes opalescent on cooling, and yields a copious precipitate on addition of a drop of dilute hydrochloric acid, acetic acid, sodium chloride, caustic soda, or sodium acetate solution: it is insoluble in alcohol. No coloration is produced by addition of iodine tincture to a solution of pure wood gum.

Wood gum is found in the wood of leafy trees, but is not present in that of conifers: the quantity of this substance in the wood of any tree increases as the axis of the trunk or branch is approached: old wood contains smaller quantities of wood gum than new wood. The following table shows the amount per cent. separated from different woods.

	Birch.	Beech (old).	Beech (young).	Do. No. 2.	Ash.	Elm.	Oak.	Cherry.
Periphery	13·9	8·2	11·9	13·8	9·7	8·9	14·4	19·3
Middle ..	19·7	15·9	11·3	15·9	10·7	12·0	10·7	15·4

M. M. P. M.

Nitroso-guanidine. By L. Jousselin (*Compt. rend.*, **88**, 814—816).—Nitroso-guanidine is prepared by passing a current of nitrous

anhydride through thoroughly dried powdered guanidine nitrate suspended in concentrated nitric acid. The salt slowly dissolves, and on adding water to the solution, crude nitroso-guanidine is precipitated in fine needles; these are separated from the mother-liquor, washed with cold water, and recrystallised from boiling water. The mother-liquor retains in solution some of the nitroso-guanidine, it being slightly soluble in dilute acids; this is recovered by neutralisation with marble and concentrating the solution.

Warm concentrated nitric acid dissolves nitroso-guanidine, and on cooling, the solution deposits a salt in pearly scales. It is also soluble in the dilute acid, and by the spontaneous evaporation of the solution, nitroso-guanidine nitrate, $CH_4N_4O.HNO_3$, separates out in large plates, identical with that obtained from the concentrated acid. It effloresces in the air, and is decomposed by water. Hydrochloric acid dissolves nitroso-guanidine, the solution yielding fine iridescent plates, which are decomposed by water. Sulphuric acid decomposes nitroso-guanidine.

When treated with concentrated caustic alkalis, nitroso-guanidine evolves ammonia gas.

By dissolving nitroso-guanidine in water, adding a drop of very dilute potash solution and a drop of ferrous sulphate solution, a beautiful purple colour is produced, which disappears after standing some time, and is discharged by acid. By treating the coloured solution with a mixture of alcohol and ether, and then with absolute alcohol, a solid deposit is formed, which, when examined under the microscope, was found to consist of dark-red crystals mixed with precipitated potassium sulphate. By the action of finely divided metallic iron on nitroso-guanidine suspended in water at 40°, a purple colour is first produced, caused by the union of the nitroso-guanidine with oxide of iron. After some time, the purple colour disappears, and is replaced by a yellow colour, ammonia gas being evolved at the same time. On cooling, nitroso-guanidine separates out, and by evaporating the mother-liquors at 60° in a vacuum, a sulphur-yellow residue remains. This body is very unstable, is soluble in water, its solution decomposing slowly at the ordinary temperature. The results of its analysis correspond with the formula CH_3N_3O, and its formation from nitroso-guanidine by the evolution of ammonia may be explained by the equation $CH_4N_4O + H_2 = CH_3N_3O + NH_3$. L. T. O'S.

Removal of Sulphur from Guanidine Thiocyanate. By S. Byk (*J. pr. Chem.* [2], **19**, 174—175).—When a limited amount of mercuric oxide is added to a hot aqueous solution of guanidine thiocyanate, ammonia is evolved, and a greyish-black compound is produced, which combines with acids to form double salts.

Analysis led to the formula $CN_3H_6Cl_5Hg_2$; apparently the new body is a double compound of two molecules of mercuric chloride with one molecule of guanidine hydrochloride. An analogous compound is produced when lead oxide is employed in place of mercuric oxide. If metallic lead be thrown into melted guanidine thiocyanate, ammonia is evolved, and lead sulphide and a new crystalline substance, $C_5N_9H_{11}O$, are produced. M. M. P. M.

Crotonaldehyde and its Homologues. By A. Lieben and S. Zeisel (*Deut. Chem. Ges. Ber.*, **12**, 570—571).—A homologue of crotonaldehyde boiling at 137°, and having the composition $C_6H_{10}O$, is formed by the action of a solution of sodium acetate on propaldehyde. This substance unites with two atoms of bromine, and also forms a crystalline compound with sodium-hydrogen sulphite. On reduction with sodium amalgam it yields a mixture of a saturated and a non-saturated alcohol. Under similar conditions, crotonaldehyde forms normal butyl alcohol and a non-saturated alcohol.

By the action of a solution of sodium acetate on a mixture of acetaldehyde with propaldehyde, a condensation product is obtained, having the composition C_5H_8O. W. C. W.

Oil of Wine. By E. Hartwig (*J. pr. Chem.* [2], **19**, 176).—This is a preliminary notice in which the author states that he has succeeded in separating the oil of wine produced in the preparation of ether into numerous components. One of these is a ketone of the empirical formula $C_8H_{16}O$. C. E. G.

α-Chlorisobutyric Acid and some of its Derivatives. By L. Balbiano (*Gazzetta chimica italiana*, **8**, 371—379).—The isobutyric acid employed was prepared by saponification of the isobutyl isobutyrate (b. p. 148—150°), obtained by the oxidation of fermentation butyl alcohol at a low temperature. The free acid, which boiled at 151—153°, was submitted to the regulated action of chlorine by passing the gas into it at a temperature of 90—95° in sunlight, in quantity sufficient to convert it into the monochlorinated derivative. As the crude product showed no signs of crystallisation at − 20°, and was decomposed by ebullition, it was converted into the ethyl salt by treatment with alcohol and hydrochloric acid. *Ethyl α-chlorisobutyrate*, $CMe_2Cl.COOEt$, when purified by careful fractional distillation, is a colourless liquid, boiling at 148·5—149·5° (corr. to 0° and 749 mm.) Its sp. gr. at 0° (to water at 0°) is 1·0619. As only one hydroxybutyric acid is obtained by decomposing the various fractions of the ethyl salt with potash, it may be inferred that only one monochlorinated acid is formed from the butyric acid under the conditions of the experiment.

Hydroxybutyric acid, $C_4H_8O_3$.—On saponifying the ethereal salt with an alkali or alkaline earth, three acids are formed: hydroxybutyric acid, an acid of the acrylic series, and dibutyllactic acid. The most convenient method of separating these is to saponify the ethyl salt with baryta, precipitate the barium as sulphate, and agitate the clear aqueous solution with ether. The dibutylactic acid is then thrown down as a white amorphous precipitate resembling alumina; the aqueous solution contains the acid of the acrylic series; and the ethereal solution, on evaporation, leaves an oily liquid which, under a desiccator, soon solidifies to a crystalline mass of hydroxybutyric acid. When collected on a vacuum filter and purified by crystallisation from water it melts at 79·3° (corr.), and sublimes at a low temperature. It forms long, slender needles, very soluble in water, in alcohol, and in ether. The

zinc salt $(C_4H_7O_3)_2Zn + 2H_2O$, crystallises in plates or small prisms, very sparingly soluble in water. It loses its water of crystallisation at 100°.

Methacrylic acid.—The acid of the acrylic series obtained from the aqueous solution appears to be methacrylic acid, from its reactions, the quantity obtained being too small to permit of an extended examination. It remains fluid at 10°, and readily unites with bromine to form a brominated compound, insoluble in water.

Dibutylactic acid, $C_8H_{11}O_5$.—The amorphous acid thrown down by ether was dissolved in water, converted into the lead salt, $C_8H_{12}O_5Pb$, by precipitation with lead acetate, and thoroughly washed: this when suspended in water and decomposed by hydrogen sulphide yielded the free acid. It is soluble in water, sparingly in alcohol, and insoluble in ether. It has not been obtained in the crystalline state, and when heated turns brown at 120°, and decomposes and melts at 150°.

The hydroxybutyric acid is identical with that obtained by Markownikoff from bromisobutyric acid, and which has been shown to have the formula $CMe_2(OH).COOH$. The methacrylic acid in all probability is formed in the following manner: $C(CH_3)_2Cl.COOEt + 2NaHO = CH_2:C(CH_3).COONa + NaCl + H_2O + EtHO$. Of the three possible formulæ for the dihydroxybutyric acid, namely:—

$CMe_2(OH).CO.O.CO.CMe_2(OH)$, $CMe_2(OH).CO.O.CMe_2.COOH$, and $CMe_2(COOH).O.CMe_2(COOH)$;

the author considers the last most likely to be correct, inasmuch as the acid is bibasic, and the conditions under which the lead salt is formed. C. E. G.

Di-substitution Derivatives of Acrylic Acid. By H. B. Hill (*Deut. Chem. Ges. Ber.*, **12**, 658—660).—In reviewing the history of these compounds, the author expresses his opinion that the formation of malonic from dibromacrylic acid affords no certain criterion of the constitution of the latter,—the ease with which bromopropiolic acid is formed, together with the observation that this acid yields, on boiling with baryta-water, bromacetylene, carbonic and malonic acids, rendering it probable that the formation of malonic acid in the former case is preceded by the elimination of hydrobromic acid.

The author has further investigated the relation of bromopropiolic acid to the acrylic series. Bromopropiolic acid is easily dissolved by hydrobromic acid at the ordinary temperature, and after some time, the solution deposits pearly plates of dibromacrylic acid (m. p. 85—86°). This acid appears to be identical with that described by Fittig and Petri.

By the action of hydriodic acid, it is readily converted into an iodobromacrylic acid (m. p. 110°); by hydrochloric acid into the corresponding chlorobromacrylic acid (m. p. 70°).

The author is further investigating the constitution of these compounds. C. F. C.

Dichloracrylic Acid. By W. Z. Bennett and H. B. Hill (*Deut. Chem. Ges. Ber.*, **12**, 655—657).—The authors have prepared this acid by

the action of aqueous alkalis from mucochloric acid (*Ber.*, **11**, 1671), for the purpose of comparison with the dichloracrylic acid of Wallach (*Ber.*, **10**, 567). Mucochloric acid was prepared by a modification of the method of Schmelz and Beilstein, viz., chlorinating pyromucic acid at 0°, by which a yield of 40 per cent. of the theoretical was obtained.

The decomposition of this acid by alkalis into formic and dichloracrylic acids takes place smoothly, yielding 85—90 per cent. of the theoretical quantity of the latter. The dichloracrylic acid thus obtained crystallises in small rhombic prisms, which sublime at the ordinary temperature. It melts at 85—86°, and at the same temperature on again heating, after rapid cooling. The melting point of β-dichloracrylic acid, on the other hand, when subjected to this treatment, sinks from 76—77° to 63—64°. It is easily soluble in water, alcohol, and ether, and in boiling benzene and ligroïn. It does not combine with bromine (below 100°).

The barium salt, $Ba(C_3HCl_2O_2)_2.H_2O$, crystallises in rhombic plates, which lose their water at 80°. One part of the salt is soluble in 16 parts of water at ordinary temperatures. The calcium salt, $Ca(C_3HCl_2O_2).3H_2O$, crystallises in concentric groups of needles, which also are dehydrated at 80°. The potassium salt crystallises in anhydrous needles; the corresponding salt of the β-acid crystallises in tables, and the formulæ of the barium and calcium salts of the same acid are $Ba(C_3HCl_2O_2)_2.6H_2O$ and $Ca(C_3HCl_2O_2)_2.1\frac{1}{2}H_2O$ respectively. These acids appear, therefore, to be distinct. The authors propose to term the former α-dichloracrylic acid. C. F. C.

Methylcrotonic and Angelic Acids. By E. Schmidt (*Deut. Chem. Ges. Ber.*, **12**, 252—258).—Having proved the identity of tiglic acid from croton oil with Frankland and Duppa's methylcrotonic acid, the author has endeavoured to ascertain the constitution of the isomeric angelic acid. The attempt to prepare this latter acid by abstracting water from hydroxyisobutylformic acid did not succeed (*Annalen*, **193**, 87); and he has therefore tried to convert it by reduction into some known variety of valeric acid. This conversion has been already effected by Ascher (*Ber.*, **2**, 685); but he did not succeed in determining the precise nature of the resulting acid.

Demarçay (*Compt. rend.*, **83**, 906) has observed that heat converts angelic into methylcrotonic acid, and the author has found that the same change is effected by time alone. A specimen of angelic acid, which had been preserved for 25 years, although retaining the outward appearance of that acid, was found to consist of pure methylcrotonic acid. The latter, by reduction, yields methylethylacetic acid with great ease; and the author's experiments show that the same body is obtained on the reduction of angelic acid.

Neither of the isomerides unites *directly* with nascent hydrogen. Hydriodic acid at 160° easily converts methylcrotonic into methylethylacetic acid; but this process does not succeed well with angelic acid. With bromine, the two acids give the same addition-product, $C_5H_8Br_2O_2$, melting at 64° (Pagenstecher, *Annalen*, **195**, 108, and this vol., p. 455); and this compound, when reduced either by sodium amalgam or by

zinc and sulphuric acid, always gives methylcrotonic acid. According to Pagenstecher, also the same *bromovaleric* acid is produced by adding hydrobromic acid to both acids.

The addition-products with hydriodic acid are, however, different. They are best obtained by introducing the finely-powdered acids into hydriodic acid of 1·96 sp. gr., cooling to 0°, and saturating with hydriodic acid gas at that temperature. After the lapse of some hours, the new acids separate. *Hydriodo-methylcrotonic acid* crystallises in fine brilliant plates (m. p. 86·5°); *hydriodo-angelic acid* separates in compact prisms (m. p. 46°), but is evidently contaminated with some other, probably isomeric, acid. If angelic acid is treated with a weaker acid than the above, a mixture of the two hydriodo-acids is produced.

To avoid intramolecular changes, both acids were crystallised at ordinary temperatures, the first from ether, the second from water, in a vacuum. Nevertheless, both yielded by reduction with zinc and sulphuric acid the same product, *methylethylacetic acid*, boiling at 173—175° (uncorr.). No difference could be detected between the acids from the two sources, or their salts. Both give methylcrotonic acid when decomposed by silver nitrate.

In its whole behaviour, angelic acid distinctly resembles β-crotonic acid; but whether it is a derivative of that acid, $CH_2 : CH.CH(CH_3).COOH$, or of methyl- α-crotonic acid, $CH_3.CH : C(CH_3).COOH$, has yet to be decided. Either formula would explain its reactions. Ch. B.

Hydroxyvaleric Acid obtained by Oxidation of Allyldimethyl Carbinol. By Semlianitzine and A. Saytzeff (*Bull. Soc. Chim.* [2], **31**, 199—200).—The constitution of this acid led the authors to suppose that by losing the elements of water, it would give rise to angelic acid: $CMe_2(OH).CH_2.COOH - H_2O = CMe_2 : CH.COOH$. Experiments confirmed this conclusion, the dehydration being effected by the action of phosphorus trichloride on ethyl hydroxyvalerate, after Frankland's method. The angelic acid was obtained in long brilliant needles (m. p. 68·5—69°), and furnished a barium salt of the formula $(C_5H_7O_2)_2Ba.2H_2O$. The author concludes from this that the hydroxyvaleric acid obtained by Miller as an intermediate product of the conversion of valeric acid (obtained from fermentation amyl alcohol) into angelic acid by oxidation, is identical with the hydroxyvaleric acid obtained from allyldimethyl carbinol. J. M. H. M.

Isomalic Acid. By M. Schmöger (*J. pr. Chem.* [2], **19**, 168—171).—Isomalic acid is produced by brominating isosuccinic acid and replacing the bromine by hydroxyl. The silver salt of the new acid, $C_4H_4Ag_2O_5$, is prepared by nearly neutralising a solution of isomalic acid with ammonia, and precipitating with silver nitrate. On heating the moist salt to about 60°, it is rapidly changed into a mass of microscopic needles of a yellow colour. The author has also obtained a crystalline zinc salt. M. M. P. M.

Synthesis of Dimethylbarbituric Acid. By E. Mulder (*Deut. Chem. Ges. Ber.*, **12**, 465—469; see also *Ber.*, **9**, 1902; and this Jour., 1878, 786).—Neither the anhydride of cyanacetic acid nor that of

malonic acid could be obtained by means of acetic chloride; but the product of the reaction of cyanacetic acid, phosphorous pentachloride, and carbon bisulphide is cyanacetic chloride, which reacts on urea with formation of cyanacetyl urea. It is a crystalline compound, sparingly soluble in water or alcohol, and melting at 200—210° without decomposition.

Cyanacetic chloride acts on dimethyl-urea with formation of cyanacetyl dimethyl urea; it can be heated to 260° without any alteration. When this urea is treated with bromine-water, a crystalline compound is obtained (m. p. 175—180°), having the same properties as the body produced by the action of bromine-water on the body (dimethylbarbituric acid) contained in the mother-liquor left in the preparation of cyanacetyl urea. The same body is also obtained by adding bromine water to the compound formed by the reaction of dimethyl urea, malonic chloride, and phosphorus oxychloride. This dimethyl (dibromobarbituric) acid has the formula, $CO<^{NMe.CO}_{N.Me.CO}>CBr_2$; it becomes red on exposure to air.

Dimethylbarbituric acid, from the mother-liquors of cyanacetyl urea, crystallises in flattened needles, soluble in water and alcohol, and can be sublimed. When acted on by strong nitric acid and brought into contact with ammonia, it becomes of a purple colour.

Cyanacetyldimethyl urea, when acted on by nitric acid, forms at least two purple compounds, one of which seems to be murexoïn; but if the urea and acid are placed over lime in an exsiccator, colourless prisms are sometimes obtained which do not consist of amalic acid.

G. T. A.

Glyoxylic Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **12**, 244—246).—When a cold concentrated solution of glyoxylic acid is neutralised with ammonia and placed in a desiccator, crystalline crusts of *ammonium glyoxylate* are deposited. These dissolve with difficulty in cold water, forming a *neutral* solution, from which calcium chloride precipitates calcium glyoxylate. On boiling the solution, large quantities of ammonia and carbonic anhydride are evolved, a brown acid liquid remaining.

If, however, alcoholic ammonia is gradually added to an alcoholic solution of the acid, a white pulverulent precipitate falls. When this precipitate is washed with alcohol and dissolved in water, and the solution evaporated over sulphuric acid, a brown uncrystallisable syrup remains, which gives a feebly alkaline solution when mixed with water. This syrup consists of *ammonium amidoglyoxylate*, since with calcium chloride it gives a precipitate of calcium amidoglyoxylate. Its aqueous solution also gives off ammonia and carbonic anhydride when boiled.

The alcoholic filtrate, when exposed to air, deposits an amorphous, deep-violet basic substance, and gives a coloured syrupy residue when evaporated.

No formulæ or analyses are given. Ch. B.

Deoxalic Acid. By H. Brunner (*Deut. Chem. Ges. Ber.*, **12**, 542—550).—By the action of sodium-amalgam on ethyl oxalate, two

isomeric modifications of ethyl deoxalate, $C_6H_5Et_3O_9$, are formed, one of which is a syrupy liquid and the other a crystalline solid.

Attempts to prepare the free acid, $C_6H_8O_9$, from the crystalline ether, by the action of sulphuretted hydrogen on its silver salt, or by adding acetic acid to its potassium salt, proved unsuccessful, since in the first case the deoxalic acid decomposed into racemic and glyoxylic acids, and in the latter it split up into Löwig's "Deoxalic acid," $C_5H_6O_8$, and acetic acid.

A diacetyl derivative, $C_6H_3(C_2H_3O)_2Et_3O_9$, is produced by the action of acetic chloride on the ethereal salt. When ammonia gas is passed into an alcoholic solution of the ethereal salt, a dark red liquid is obtained which on evaporation yields a hygroscopic reddish-brown amorphous powder having the composition $C_6H_{12}N_4O_5 + H_2O$.

A small quantity of the syrupy β-modification of ethyl deoxalate, which had remained under a bell-jar for several years, deposited crystals of tartronic acid.

The author represents the constitution of the two isomeric deoxalic acids thus:—

α COOH.CH(OH).O.CH(COOH).CH(OH).COOH.

β $COOH.C(OH)<\begin{matrix}CH(OH).COOH\\CH(OH).COOH\end{matrix}$ W. C. W.

Constitution of Parabanic Acid. By A. Calne (*Deut. Chem. Ges. Ber.*, **12**, 624—625).—The constitution of parabanic acid was hitherto problematical, from the fact that oxaluric acid could lose 1 mol. H_2O in a number of different ways. The usually accepted formula, $CO<\begin{matrix}NH—CO\\|\\NH—CO\end{matrix}$, differs from all the other possible expressions of their dehydration, in the symmetrical disposition of its hydrogen atoms.

The resolution by the action of acids of the corresponding dimethyl-derivative, cholestrophane, affords therefore a ready criterion of its trustworthiness. With this view the author subjected it to the action of hydrochloric acid at 200°, and found, in effect, that it split up into carbonic and oxalic acids and *pure methylamine*, no trace of ammonia being formed.

The above formula appears, therefore, to be the true expression of the constitution of this acid. C. F. C.

Note.—The author has probably overlooked the fact that diphenyl-parabanic acid is known to be resolved, by the action of potash, into oxalic and carbonic acids and phenylamine (Hofmann, *Proc. Roy. Soc.*, **11**, 275). C. F. C.

Action of Aluminium Chloride on Acetic and Sulphuric Anhydrides. By A. Andrianowsky (*Bull. Soc. Chim.* [2], **31**, 199).—Aluminium chloride acts on acetic anhydride in the cold with formation of acetic chloride and aluminium acetate. The reaction of aluminium chloride with sulphuric anhydride takes place at 50—60°, and results in the formation of a compound having the formula $AlCl_2.SO_2Cl$. At a higher temperature, this compound is decomposed

with evolution of sulphuric anhydride. Its action on benzene is attended with separation of hydrochloric acid, and is more energetic in presence of aluminium chloride. J. M. H. M.

Chemical Functions of Acetic Anhydride. By Loir (*Compt. rend.*, **88**, 812—813).—The author compares the properties of acetic anhydride with those characteristic of the aldehydes.

(1.) *By the Action of Reducing Agents, Acetic Anhydride yields Alcohol.*—On subjecting acetic anhydride to the action of sodium amalgam for three days and distilling the product with water, a large quantity of acetic ether distils over, together with an acid liquid; and this by repeated distillation over potash yields a neutral liquid, from which alcohol may be separated on addition of potassium carbonate.

(2.) *Acetic Anhydride forms a Crystalline Compound with Sodium Hydrogen Sulphite.*—On mixing a solution of sodium hydrogen sulphite at 0° with acetic anhydride, heat is evolved without the escape of sulphurous anhydride, and on keeping the solution at 0°, crystals separate out, which dissolve with evolution of sulphurous anhydride if the temperature be raised. They are soluble in water, and are decomposed by it, forming acetate and sulphite of sodium.

(3.) *Acetic Anhydride forms a Crystalline Compound with Ammonia insoluble in Ether.*—On adding acetic anhydride to ether saturated with ammonia at −26°, and keeping the solution at that temperature, crystals separate out; these dissolve on raising the temperature, and on evaporating the solution a residue of acetamide remains. The crystals are insoluble in absolute ether at −20°, but are decomposed by water, forming a strongly acid solution.

(4.) *Acetic Anhydride has an Affinity for Oxygen.*—Acetic anhydride when free from acetic chloride reduces silver nitrate, forming a mirror when heated with it in ammoniacal solution.

These reactions show that acetic anhydride may be considered as an ether and an aldehyde. L. T. O'S.

Formation of Glycocine from Ethyl Nitro-acetate. By de Forcrand (*Compt. rend.*, **88**, 974—976).—By the action of silver nitrite on ethyl bromacetate, a liquid is obtained boiling between 151° and 152°, having the sp. gr. 1·133 at 0°; its odour resembles that of ethyl nitrite. The analyses agree with the formula for ethyl nitro-acetate, $C_2H_2(NO_2)O_2.C_2H_5$. By the action of reducing agents on this body, ethyl amido-acetate, $C_2H_2(NH_2)O_2.C_2H_5$, is formed, from which glycocine may easily be obtained. L. T. O'S.

Boron Compounds. By C. Councler (*J. pr. Chem.* [2], **18**, 371—402).—Most of the facts mentioned in the paper have already appeared in abstract in this Journal (1876 [ii], 394, and 1878, Abst., 21 and 774).

Action of Zinc Ethide on Allyl Borate.—The author was in hopes that in this reaction boron triallide would be formed as follows, $B(C_3H_5O)_3 + 3ZnEt_2 = B(C_3H_5)_3 + 3(ZnEt.EtO)$. The two compounds react easily on one another, and the product when distilled in a current of carbonic anhydride yields a liquid distillate and a crys-

talline residue: the latter is decomposed by water with evolution of gas, apparently ethane. The liquid usually contains zinc-ethyl, from which it cannot be freed by fractional distillation: in one instance only was a colourless liquid of high refractive power obtained free from zinc. It boiled at about 110—120°, and on analysis was found to have the composition of *boron glycide*, BC_3H_5. C. E. G.

Iodides of Stannopropyl. By A. Cahours (*Compt. rend.*, **88**, 725—727).—In a previous paper (*Compt. rend.*, **76**), the author states that by the action of an alloy of tin and sodium on propyl iodide at 100° for several days he obtained a crystalline body resembling iodide of stanno-stannic ethyl, and which he supposed to be stanno-stannic propiodide.

This body on addition of ammonia yields a white amorphous precipitate resembling stannous ethyl in its properties: it dissolves in hydrochloric acid, forming a crystalline chloride. By distilling the iodide with potash, a liquid is obtained which solidifies on cooling, whilst an amorphous residue is left behind. The distillate is a mixture of *stannic di-iodo-dipropylide* and *stannic iodo-tripropylide*.

To obtain the latter compound pure, propyl iodide is treated with an alloy of tin and sodium (containing 16 per cent. of the latter metal) in the powdered state. A considerable development of heat is produced by the reaction, and after heating for several hours with inverted condenser, the mass solidifies; this is exhausted with ether, and the residue, after expulsion of the latter, yields *stannic iodo-tripropylide* on distillation. It is a liquid boiling between 262—264°, and when distilled with potash yields a liquid, which on cooling solidifies to a mass of prismatic crystals of a powerful odour. These unite with hydrochloric acid, forming the corresponding chloride, a heavy colourless oil with an irritating odour.

Whilst on the one hand, *stannic diiodo-diethide* has a higher melting point than the corresponding methyl compound, on the other hand *stannic diiodo-dipropylide* remains liquid at −20°: the corresponding chlorine compound, however, is a solid melting at 80°.

L. T. O'S.

Formation of Organic Ultramarines. By de Forcrand (*Bull. Soc. Chim.* [2], **31**, 161—166).—Inasmuch as it appears to be possible to produce an ultramarine from any metal by heating yellow silver ultramarine, prepared according to Heumann's direction (*ibid.*, **28**, 570), with a metallic chloride, it seemed not improbable that an organic ultramarine might be produced by substituting for a metallic chloride the chloride or iodide of an alcohol radicle. With this end in view, silver ultramarine was enclosed in a sealed tube with excess of ethyl iodide, and heated for 50 or 60 hours at 180°; a clear grey or greyish-yellow powder was thus obtained, containing no silver, which disengaged easily even at 100° a little ethyl sulphide. On heating it more strongly, ethyl sulphide was abundantly evolved, together with other products of decomposition, such as sulphur dioxide, but when it was intimately mixed with sodium chloride and very carefully heated, scarcely any ethyl sulphide escaped, whilst the mixture, previously grey, became blue, reproducing ordinary ultramarine. Under these

circumstances, ethyl chloride is abundantly disengaged, the reaction being exactly comparable with the formation of silver chloride when silver ultramarine is treated with sodium chloride.

The ultimate analysis of the new compound showed a considerable excess of carbon above that which theory required, a result probably due to the formation of secondary products in the original reaction, or perhaps to a separation of elementary carbon, from neither of which could the ultramarine be purified.

In order to prove the presence of ethyl in the organic ultramarine, a weighed quantity of the latter was carefully heated, and the sulphide evolved was passed into solution of mercuric chloride: the analysis of the combination agreed accurately with the formula $Et_2S.HgCl_2$.

Similar ultramarines were prepared by the action of amyl, allyl, and benzyl iodides, but the two former could not be obtained free from silver; they resembled in all their reactions the ethyl compound above described. J. W.

Action of Iodine on Aromatic Compounds with Long Side-Chains. By K. Preis and B. Raymann (*Deut. Chem. Ges. Ber.*, **12**, 219—224).—The action of iodine on various oils of turpentine has been investigated by Kekulé, Oppenheim and Pfaff, and others; all of whom found cymene to be one of the principal products. In the experiments here described, that portion of "Wiener-Neustädter Terpentinöl" (from the firm of Rössler, in Prague), which boiled at 152—154° was used, having been previously washed with caustic soda to remove resinous matter. The oil, mixed with half its weight of iodine, was heated at 230—250° for twelve or fourteen hours. On opening the tubes, much gas was given off, consisting probably of hydrocarbons belonging to the methane series. The contents of the tubes when treated with caustic soda yielded an oily layer of hydrocarbons, which was removed and rectified. This liquid began to boil at 70°, and at 330° decomposition set in. The greater part of it distilled between 165—175°, and between 180—220°.

Fraction 70—112° probably contained *hydrides of toluene* and *xylene*. Fraction 108—112° gave a little terephthalic acid when oxidised with chromic mixture.

Fraction 138—143° gave, when nitrated, a compound melting at 176°, probably $C_8H_7(NO_2)_3$. When oxidised it gave isophthalic and a little terephthalic acid. Hence it contained *metaxylene* and a little *paraxylene*.

Fraction 155—165° contained no propyl-benzene, since it gave no benzoic acid when boiled with dilute nitric acid. It contained *mesitylene* and *pseudocumene*, which were separated as sulphonamides (Jacobsen, *Ber.*, **9**, 256), and gave a bromine compound, $C_9H_9Br_3$, melting at 219°.

Fraction 173—178° (an exceedingly small one) smelt of cymene, but did not give its characteristic sulphonic acid. It probably contained *cymene hydride*.

Fraction 189—193° contained a benzene derivative with eleven carbon-atoms. This was not Fittig's "Laurol" (*Annalen*, 145—150), since it gave a bromine compound, $C_{11}H_{13}Br_3$, melting at 205°.

Fraction 270—300° contained *polyterpenes*.

The authors explain the absence of cymene from these products by supposing that it is at first formed, but is subsequently converted by the iodine and hydriodic acid into other bodies. They find in fact that when cymene is digested at 280° with half its weight of iodine, it yields a series of hydrocarbons containing from eight to twelve atoms of carbon. This action differs from the exhaustive chlorination and bromination of aromatic hydrocarbons (Ruoff, *Ber.*, **11**, 1048 and 1480; Gessner, *ibid.*, **11**, 1505; Gustavson, *ibid.*, **10**, 1101, and **11**, 1251) only in this, that the separated side-chains react on the benzene nucleus producing higher hydrocarbons; as in Schützenberger's synthesis of benzyl-toluene by the action of iodine on toluene (*Compt. rend.*, **75**, 1767), or Hofmann's conversion of methylaniline into toluidine. An analogous case is presented by the action of zinc chloride on camphor (Fittig, *Annalen*, **145**, 129). Ch. B.

Isocymene (Paramethylcumene). By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **12**, 429—434).—Parabromocumene is prepared by the action of bromine in the cold on cumene from cumic acid (Mensel, *Inaug. Dissert.*, Gottingen, 1867, 29). It is a colourless liquid, of sp. gr. 1·3014 at 15°, which does not solidify at −20°, and boils at 217°. Isocymene is formed from this compound by treating its ethereal solution with sodium and methyl iodide. Isocymene is a liquid which boils at 171—172° (bar. 765 mm.), and does not solidify at −20°: with the same thermometer, cymene was found to boil at 175—175·5°. The sp. gr. of isocymene at 0° is 0·8702, that of cymene being 0·8718. Isocymene by oxidation is converted into terephthalic acid.

Sulphuric acid acts on isocymene as on cymene, forming two sulphonic acids, which may be separated by means of their barium salts. The salt of the acid formed in larger quantity separates first, and crystallises from water in fine needles united in stellate groups. It has the composition $(C_{10}H_{13}SO_3)_2Ba + H_2O$, and differs from barium cymene-sulphonate in the amount of water of crystallisation, in crystalline form, and in its solubility in water. The copper salt of this isocymene-sulphonic acid is an easily soluble salt, crystallises in large light blue rhombic plates having the composition $(C_{10}H_{13}SO_3)_2Cu + 4H_2O$. The copper cymene-sulphonate also crystallises with $4H_2O$, but forms ill-defined crystals only. Sodium isocymene-sulphonate forms easily soluble leafy crystals; by the action of phosphorus pentachloride and treatment of the acid chloride with ammonia, it is converted into the sulphamide, which is easily soluble in alcohol, insoluble in cold, but soluble in hot water and in ammonia. From its hot aqueous solution, it separates in large iridescent crystals resembling those of cymene sulphamide (m. p. 97—98°). Hydrochloric acid at 200° regenerates the hydrocarbon. Sodium isocymene-sulphonate when fused with soda yields a phenol sparingly soluble in water, and resembling carvacrol in odour. Its aqueous solutions yield no coloration with ferric chloride. By long continued fusion with soda, hydroxyterephthalic acid and a monobasic hydroxyacid volatile in aqueous vapour are formed. This hydroxycumic acid crystallises from its hot aqueous solutions in small flat prisms, from alcoholic solutions in large soft plates (m. p. 88°). In its behaviour towards solvents and precipitants

it resembles isohydroxycumic acid (m. p. 93°) prepared from carvacrol (*Ber.*, **11**, 1061). With ferric chloride, its solutions give an intense reddish-violet coloration. Its barium salt is soluble in water, and forms hard short prisms resembling barium isohydroxycumate. The excessively soluble barium salt of the second sulphonic acid formed by the action of sulphuric acid on isoxymene is obtained as a tenacious mass by evaporating the mother-liquors of the first, but becomes crystalline on standing. Its copper salt forms a light blue mass. Its sulphamide separates from hot aqueous solutions as a liquid which solidifies to a scaly mass on standing; it melts between 80° and 90°. By fusion of the sodium salt with potash, a hydroxy-acid (m. p. 166—170°) is obtained, whose aqueous solutions yield a bluish-violet coloration with ferric chloride.

From the analogy between the products formed by the fusion of carvacrol and thymol with potash, the author concludes that the constitutions of the two isocymene-sulphonic acids and the monobasic acids derived from them are as follows. 1st. Sulphonic acid, $Me : SO_3H : CHMe_2 = [1 : 2 : 4]$. 2nd acid, $Me : SO_3H : CHMe_2$ $[1 : 3 : 4]$. Hydroxycumic acid, $COOH : OH : CHMe_2$ $[1 : 2 : 4]$. Metabromosalicylic acid, $Me : OH : COOH$ $[1 : 3 : 4]$.

The fact that the isocymene prepared from the sulphamide (m. p. 97—98°) yields the two sulphonic acids, shows that the second sulphonic acid is derived from the same hydrocarbon as the first.

The barium salts of the sulphonic acids offer the best means of distinguishing between cymene and isocymene. Since the preparation of cymene from cumic alcohol (Kraut, *Annalen*, **192**, 225) is not in accordance with the author's views on the constitution of the propyl group in cymene, he has examined cymene so prepared by means of the barium salts of the sulphonic acids, and finds it to be perfectly free from isocymene. Hence paramethylcumene is different from cymene, but the formation of cymene from cumic alcohol leads to the conclusion that in the distillation with zinc-dust a molecular change takes place in the propyl group. P. P. B.

Presence of Metanitrotoluene in Commercial Nitrotoluene. By F. Monnet, F. Reverdin, and E. Nölting (*Deut. Chem. Ges. Ber.*, **12**, 443—445).—By oxidising commercial nitrotoluene (b. p. 225—230°) with potassium permanganate, the authors obtained a mixture of nitrobenzoic acids, from which they have succeeded in separating an acid (m. p. 138—140°) agreeing in all its other properties with metanitrobenzoic acid. Hence they conclude that metanitrotoluene is present in the commercial product. P. P. B.

Influence of Metatoluidine in the Preparation of Rosaniline. By P. Monnet, F. Reverdin, and E. Nölting (*Deut. Chem. Ges. Ber.*, **12**, 445).—The authors having found that metatoluidine is present in commercial toluidine, have investigated its effect on rosaniline colours formed in its presence. The results obtained show that it injures the purity of the colour.

Oxidised base.	Shade of colour produced.
Metatoluidine	Brown.
Metatoluidine + aniline	Violet.
Meta- + paratoluidine	Brown.
Meta- + orthotoluidine	Red, violet, and greyish.
Meta- + orthotoluidine + aniline	Red, yellow, and greyish.
Meta- + paratoluidine + aniline	Red, slightly violet, and greyish.

P. P. B.

Nitrodimethyl-aniline. By C. Wurster (*Deut. Chem. Ges. Ber.*, **12**, 528—530).—The nitrodimethyl-aniline which Schraube (*Ber.*, **8**, 621) prepared by the action of potassium permanganate on nitrosodimethyl-aniline hydrochloride, and the nitrodimethyl-aniline obtained by Weber (*Ber.*, **7**, 714, and **10**, 761) are identical. Each has the same melting point, 162°, and yields dimethyl-paraphenylene-diamine on reduction with tin and hydrochloric acid. Nitrodimethyl-aniline does not form salts. W. C. W.

Dimorphism of 1 : 4 Acetotoluide. By R. Panebianco (*Gazzetta chimica italiana*, **8**, 426—429).—The crystals left on the spontaneous evaporation of the alcoholic solution belong to the monoclinic system—

$$a : b : c = 1{\cdot}21654 : 1 : 0{\cdot}78885\,;\ \eta = +\mathrm{X} : +\mathrm{Z} = 106^\circ\ 7'\ 20''.$$

The observed forms were (100), (001), (110), ($\bar{1}11$), (011), (021). Cleavage planes parallel to (001), perfect; parallel to (100), less perfect, making between them an angle of 73° 52′ 40″. The plane of the optical axes is parallel to the plane of symmetry. The angle of the optical axes in oil is 106° 10′; ($\rho < v$) for the red.

The prismatic crystals deposited on cooling the solution belong to the trimetric system $a : b : c = 0{\cdot}65147 : 1 : 0{\cdot}32885$. The observed forms were (100), (010), (001), (110), (101), (121). The cleavage could not be ascertained. The plane of the optical axes is parallel to (010). In the dispersion $\rho > v$ and $2\mathrm{H}_\alpha = 84^\circ\ 00'$ for the red. It is remarkable that the three known cases of dimorphism belong to the aromatic series with position 1 : 4. C. E. G.

Methyl-derivatives of Paraphenylene-diamine. By C. Wurster (*Deut. Chem. Ges. Ber.*, **12**, 522—528).—Nitrosodimethylaniline, prepared by adding sodium nitrite to a mixture of dimethylaniline and hydrochloric acid, is reduced by the action of tin and hydrochloric acid. When the operation is completed, the tin double salt separates out. A further yield may be obtained by saturating the mother-liquor with hydrochloric acid gas. The free base, *dimethylparaphenylene-diamine*, which separates out as a brown oil when the tin salt is gradually added to an excess of warm soda-lye, is dried over calcium chloride and distilled. On cooling this distillate, the base crystallises out, and the crystals, after being pressed between filter paper, are dissolved in a small quantity of warm benzene. On cautiously adding warm petroleum ether to this solution, an oil separates out, which contains all the impurities. Cold petroleum ether is now added, when the dimethylphenylene-diamine separates out in long white

needles resembling asbestos in appearance. The pure base does not undergo any change on exposure to the atmosphere; the impure compound, however, acquires a red or violet colour. Dimethylparaphenylene-diamine melts at 41° and boils at 257°. It dissolves freely in water, alcohol, benzene, and chloroform, but is less soluble in ether and in light petroleum.

Acetyldimethylparaphenylene-diamine, $NMe_2.C_6H_4.NH.\bar{A}c$, forms white needles or plates (m. p. 130°), soluble in benzene, alcohol, and hot water. It boils at 355° with slight decomposition.

Tetramethylparaphenylene-diamine, $NMe_2.C_6H_4.NMe_2$, first obtained by Hofmann (*Jahresber.*, 1863, 422) by the action of methyl iodide on the dimethylated base, was prepared by heating a mixture of dimethylphenylene-diamine with methyl alcohol and hydrochloric acid in sealed tubes, first at 180° and subsequently at 200°. On adding soda to the crude product, an oil separates out, which after purification by distillation and crystallisation from dilute alcohol, deposits tetramethylparaphenylene-diamine in white plates. It melts at 51°, and boils without decomposition at 260°. The base dissolves in hot water and in the usual solvents. Oxidising agents produce an intense blue coloration in solutions of the base. The hydrochloride, sulphate, and platinum double salt of tetramethylphenylene-diamine dissolve readily in water. W. C. W.

Action of Ethyl-oxalate on Dimethylparaphenylene-diamine. By R. Sendtner (*Deut. Chem. Ges. Ber.*, **12**, 530—533).—When dimethylphenylene-diamine is heated with rather more than one equivalent of ethyl oxalate, a mixture of ethylic dimethylphenylene-diamine-oxamate and diparamidodimethylphenyl-oxamide is formed. The product of the reaction is treated with ether to remove the excess of ethyl oxalate, and the residue is digested with warm alcohol, which dissolves out the oxamate and leaves the anilide.

Dimethylparaphenylenediamine-oxamic acid,

$$N.Me_2.C_6H_4.NHCO.COOH,$$

crystallises in grey needles or plates, which dissolve freely in water, but only sparingly in boiling alcohol. The acid melts at 192°, with decomposition. The *ethyl salt* crystallises in yellow needles or plates (m. p. 117°), soluble in hot water and in hot alcohol. It is soluble in acids, forming crystalline salts. On adding alcoholic ammonia to an alcoholic solution of this ethereal salt, *monoparamidodimethylphenyl-oxamide*, $NMe_2.C_6H_4.NHCO.CONH_4$, crystallises out (m. p. 257—259°). This substance is soluble in hot benzene. It unites with acids to form crystalline salts, which dissolve in hot water.

Diparamidodimethylphenyl-oxamide, $[CONH.C_6H_4.NMe_2]_2$, forms a yellow crystalline powder, which does not melt when heated to 270°. It is soluble in boiling benzene and chloroform. Its salts dissolve readily in water. W. C. W.

Dimethylparaphenylenediamine-carbamides. By F. Binder (*Deut. Chem. Ges. Ber.*, **12**, 535—537).—The *dicarbamide*,

$$CO(NH.C_6H_4.NMe_2)_2,$$

is formed by heating 1 part of urea with 4 parts of dimethylparaphenylenediamine at 130—150° for three hours. The crude product is washed with alcohol, and is purified by conversion into the sulphate. The dicarbamide crystallises in long needles soluble in boiling acetone. It melts at 262°, with decomposition. The *sulphate*, $C_{17}H_{22}N_4O.H_2SO_4$, is sparingly soluble in water, and the *hydrochloride*, $C_{17}H_{22}N_4O.2HCl$, is very soluble.

The *monocarbamide*, $NH_2.CO.NH.C_6H_4.NMe_2$, obtained by mixing solutions of potassium cyanate and dimethylparaphenylenediamine, forms large white needle-shaped crystals (m. p. 179°) soluble in boiling water. The sulphate and hydrochloride are easily soluble.

W. C. W.

Dimethylparaphenylenediamine-thiocarbamide. By A. Baur (*Deut. Chem. Ges. Ber.*, **12**, 533—535).—*Dimethylparaphenylenediamine-thiocarbamide*, $CS(NH.C_6H_4.NMe_2)_2$, obtained by boiling the diamine with carbon bisulphide, is a white crystalline powder (m. p. 186·5°), soluble in hot benzene and in hot alcohol. The hydrochloride, $C_{17}H_{22}N_4S.2HCl$, is a white crystalline powder soluble in alcohol. The acetyl derivative crystallises in white glistening plates (m. p. 71°).

W. C. W.

Colouring Matter containing Sulphur derived from Dimethylphenylenediamine. By A. Koch (*Deut. Chem. Ges. Ber.*, **12**, 592—595).—The blue colouring matter which is formed by treating dimethylphenylenediamine first with sulphuretted hydrogen and then with ferric chloride, is precipitated by zi ncchloride, and may be purified by dissolving it in water and reprecipitating with zinc chloride. When hydrochloric acid is added to an aqueous solution of the blue compound, dark blue plates of an intense metallic lustre slowly separate out. The crystals contain from $1\frac{1}{2}$ to 4 molecules of water, and have the composition $C_{16}H_{18}N_4S.HCl$. The compound is soluble in water and alcohol; it is bleached by reducing agents, and is precipitated by potassium dichromate, zinc chloride, or mercuric chloride. When sulphuretted hydrogen is passed through an ammoniacal solution of the blue compound, a yellow precipitate is formed, which turns green on exposure to the air.

On evaporating the liquid from which the blue colouring matter has been precipitated by zinc chloride, bronze-coloured needles separate out, which have the composition $C_{16}H_{18}N_4S_4.2HCl.ZnCl_2 + 2H_2O$. This substance is soluble in water and alcohol. It is precipitated by mercuric chloride, and is bleached by alkalis.

The formation of the blue compound is represented by the following equation: $2C_8H_{12}N_2 + H_2S + 2O_2 = C_{16}H_{18}N_4S + 4H_2O$, and that of the red colouring matter thus: $2C_8H_{12}N_2 + 4SH_2 + 7O = C_{16}H_{18}N_4S_4 + 7H_2O$.

W. C. W.

Oxidation of Orthotoluene Sulphonamide. By C. Fahlberg and I. Remsen (*Deut. Chem. Ges. Ber.*, **12**, 469—573).—This is the continuation of former experiments (*Annalen*, **178**, 293). When orthotoluene sulphonamide is oxidised by permanganate, a body is obtained for which the authors propose the name *anhydrortho-*

sulphamine-benzoic acid, although it is not really either an acid or anhydride.

It consists of $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH$, and easily yields the salts of ortho-sulphamine benzoic acid. It dissolves in hot water, alcohol, and ether. It melts at 220° (uncorr.), with partial decomposition. It has a very sweet taste, exceeding that of cane-sugar. When fused with potash, it is entirely converted into salicylic acid. Phosphorus pentachloride has no action on it. The ethyl ether could not be prepared in the ordinary way. When an aqueous solution of the new compound is neutralised by metallic carbonates, salts are obtained which have the composition of salts of sulphamine-benzoic acid. Stronger acids precipitate from these salts anhydrosulphamine-benzoic acid and not sulphamine-benzoic acid.

The *barium* salt, $[C_6H_4(SO_2.NH_2).COO]_2Ba,4\frac{1}{2}H_2O$, is very soluble, and crystallises in brilliant concentrically grouped needles. The *magnesium* salt crystallises with $6\frac{1}{2}H_2O$ in long, transparent needles. The *lead* salt forms a syrupy mass. The *sodium*, *potassium*, and *ammonium* salts are very soluble, and crystallise in small needles. All the salts have a sweet taste. Besides this acid, orthotoluenesulphonamide yields on oxidation an acid potassium salt of orthosulphobenzoic acid, which remains behind when the new acid has been precipitated. This salt crystallises in large monoclinic tables; it is easily converted into salicylic acid by fusion with potash. Probably two molecules of orthotoluene-sulphonamide give rise to one molecule each of orthosulphamine-benzoic acid and orthosulphobenzoic acid. The formation of sulphobenzoic acid on oxidation of toluenesulphonamide is analogous to the formation of sulpho-isophthalic acid, on oxidation of sulphamine-metatoluylic acid (*Ber.*, **11**, 2087). The anhydro-acid is converted into the orthosulpho-acid by heating with concentrated hydrochloric acid at 150°, in sealed tubes. The sulpho-group could not be replaced by hydrogen to form benzoic acid, nor could benzoic acid be obtained from parasulphamine-benzoic acid.

Orthosulphobenzoic acid, $COOH.C_6H_4.SO_2.NH_2$, melts at 240°, and is not deliquescent. The acid *barium* salt contains $2\frac{1}{2}H_2O$, and crystallises in needles.

Orthosulphobenzoic acid is converted into anhydrosulphamine-benzoic acid by the action of phosphorus pentachloride on the neutral potassium salt, addition of ammonia and hydrochloric acid. The authors failed to convert the orthosulphobenzoic acid into phthalic acid by the action of sodium formate. G. T. A.

Remarks on Weselky's and Bendikt's Investigation "on some Azo-compounds." By P. Griess (*Deut. Chem. Ges. Ber.*, **12**, 426—428).—Weselky and Benedikt's (*Ber.*, **12**, 226) azo-benzene-naphthylamine was long ago described by the author (*Phil. Trans.*, 1864, 674) under the name of diazobenzene-amidonaphthol, but he is still uncertain whether to regard it as an azo- or diazo-compound. The base cannot be used as dye owing to its insolubility; its sulphonic derivative, $C_{16}H_{13}N_3SO_3$, may, however, be used to dye a reddish-yellow. It may be prepared by treating an aqueous solution of

naphthylamine hydrochloride, with an equivalent quantity of diazobenzenesulphonic acid (prepared from sulphanilic acid). The sulphonic acid crystallises in microscopic brownish-violet needles, sparingly soluble in water. It forms well crystallised salts; alkalis colour its dilute solutions orange, whilst mineral acids produce a magenta coloration. The formation of this body may be used as an extremely delicate test for nitrous acid; to this end a solution containing traces of the latter is treated with sulphuric acid, and sulphanilic acid is then added; after standing ten minutes a colourless solution of naphthylamine sulphate is added, and in a short time the solution turns magenta. This test may be used to demonstrate the presence of nitrites in saliva. Even aided by this, the author has failed to corroborate Schonbein's statement that nitrites occur in the urine. Further, the author corrects the error of Weselky and Benedikt in attributing to Kekulé and Hidegh (*Ber.*, **3**, 233) the discovery of oxyazobenzene, which the author had already prepared in 1864 (*loc. cit.*), and by a second method five years later (*Annalen*, **154**, 212). P. P. B.

Azo-, Azoxy-, and Hydrazo-Compounds. By H. Schmidt and G. Schultz (*Deut. Chem. Ges. Ber.*, **12**, 482—486).—The best method of preparing benzidine is by the direct addition of azobenzene in alcoholic solution to stannous chloride and hydrochloric acid. Azoxybenzene is converted almost entirely into aniline by stannous chloride. For the preparation of large quantities of azobenzene, it is best to prepare azoxybenzene first from nitrobenzene, alcoholic solution of potash, and alcohol. The formation of hard resinous bodies may be lessened by addition of zinc-dust, or granulated zinc. The azoxybenzene may be purified by distilling off the aniline, &c., and pouring the residue into water. The crystalline mass so obtained is freed by acids from any trace of aniline, and warmed in alcoholic solution with fuming nitric acid. To convert it into azobenzene, it is mixed with iron filings and distilled.

The conversion of azoxybenzene into aniline by stannous chloride is explained by supposing that an intermediate hydrazoxybenzene, $C_6H_5.NH.O.NH.C_6H_5$, is formed, which splits up into two molecules of aniline. This view is supported by the existence of certain compounds obtained by Hofmann and Geyger (*Ber.*, **9**, 169), from chloronitrobenzene and sodium, and by the action of benzoic chloride on the bodies so obtained. It is also supported by experiments of the authors which show that by the action of acetic anhydride, the two hydrogen atoms of hydrazobenzene can be replaced by acetyl, giving rise to diacetylhydrazobenzene. The product is a yellow resinous body, which soon becomes brittle, but can be obtained in large, transparent crystals, of a faint yellow colour, by crystallisation from alcohol. It is sparingly soluble in water, and melts at 103°. Concentrated hydrochloric acid converts it into benzidene.

The following table gives a few instances of the melting points of azo-, &c., compounds:—

	Nitro-product.	Azoxy-product.	Azo-products.	Hydrazo-product.	Amido-product.	Diphenyl-base.
Benzene	3°	37°	68°	131°	8°	122°
Bromo- { meta	56	111·5	125·5	107—109	18—18·5	152
benzene { para	127	175	205	130	64	?
Chloro- { meta	45	97	101	94	liquid	163
benzene { para	83	155—156	183	122	70—71	?

G. T. A.

Propylphenols, and other Derivatives of Propylbenzene. By P. Spica (*Gazzetta chimica italiana*, **8**, 406—426).—Although on comparing the known facts relating to the constitution of cymene from various sources, and that of the cuminic derivatives, most of them indicate that the side-chain in the cumene derivatives is propyl, whilst that of the others is isopropyl, yet there are other facts which are not in harmony with this supposition. Amongst these the following may be mentioned:—1. The formation of isopropyl bromide and pentabromotoluene by the action of bromine on cymene (Gustavson, *Ber.*, **10**, 1101). 2. The excretion of an acid, having the composition and fusing point of cumic acid, by the oxidation of cymene in the animal organism, as observed by Nencki and Ziegler (*Ber.*, **5**, 749). 3. The transformation of cumic alcohol into a hydrocarbon which Kraut (*Annalen*, **192**, 222) found to be identical with ordinary cymene. 4. The formation of the same isopropylbenzene from benzene by the action of either isopropyl or propyl bromide in presence of aluminium bromide (Gustavson, *Ber.*, **11**, 1251). Whether the supposition that a molecular transposition takes place in the cases cited affords a satisfactory explanation of these anomalies, remained undecided, and the author was consequently induced to study the derivatives of synthetical propylbenzene, so as to remove any doubt as to the nature of the C_3H_7 group in cumene. Propylbenzene was prepared by Fittig, Schaeffer and Koenig's method of acting with sodium on a mixture of bromobenzene and propyl iodide, diluted with ether. The propylbenzene—which is produced in small quantity only by this method—when separated from the diphenyl, hexane, &c., formed at the same time, boils at 157·6—159° (corr. to 0° and 758 mm.), and has a density of 0·88009 at 0°. The propylbenzene, prepared by the action of zinc ethide on benzyl chloride (Paternò and Spicà, *Gaz.*, **7**, 22, and this Jour., 1877 [i], 707), boils at 156·5—158·5°, and has a density of 0·881. Cumene, however, boils at 151—151·5°, and has a density of 0·8797 (Paternò and Pisati, *Gaz.*, **3**, 574).

When oxidised with dilute nitric acid, the propylbenzene is converted into paranitrobenzoic acid (m.p. 238°). Heated with a mixture of fuming and ordinary sulphuric acid, and subsequently diluted and neutralised with barium carbonate, it yields the barium salts of two sulphonic acids, identical in every respect with those formerly obtained from the propylbenzene prepared by the action of zinc ethide on benzyl chloride (*loc. cit.*)

α-Propylphenol, $C_6H_4(C_3H_7).OH$. The less soluble α barium salt is

converted into a potassium salt and fused with potash. The phenol, extracted in the usual way by acidifying the solution of the fused mass and agitation with ether, is a colourless oily liquid, boiling at 230·6—232·6° (corr. to 0° and 758·56 mm.). The α-propylphenol formerly obtained (*loc. cit.*) boiled at 230°. Cumophenol boils at 228·2—229·2° (corr. to 0° and 758·18 mm.) α-Propylphenol is sparingly soluble in water, and the solution, on addition of ferric chloride, acquires a faint violet tinge, changing to greenish after some time. It has a density of 1·0091 at 0° and 0·9324 at 99·8°, and does not solidify in a mixture of ice and salt. Cumophenol is a solid, melting at 61°. The *acetyl* derivative, $C_6H_4(C_3H_7).OAc$, prepared by the action of acetic chloride on α-propylphenol is a colourless liquid (b. p. 242·7—244°, corr. to 0° and 760·15 mm.), which is decomposed by boiling with potash solution. Density at 0° = 1·02904; at 100° 0·94229. The *methyl ether*, $C_6H_4(C_3H_7).OMe$, obtained by the action of potash on a solution of the phenol and iodomethane in methyl alcohol, is a highly refractive liquid of pleasant odour, resembling that of aniseed. It boils at 214—215·5° (corr. to 0° and 750·18), and its density is 0·96364 at 0° and 0·91251 at 99·6. As this methyl ether, when oxidised with chromic mixture, yields anisic acid (m. p. 176°)—a para-compound—the α-propylphenol is *parapropylphenol* $OH : C_3H_7 = [1 : 4]$, and the corresponding sulphonic acid *parapropylbenzenesulphonic acid.*

Parapropylphenolcarbonic acid, $C_6H_3(C_3H_7)(OH).COOH$, is prepared by the simultaneous action of carbonic anhydride and sodium on para-propylphenol at 140°: the product of the reaction is treated in the usual way, first with excess of hydrochloric acid, and then with ammonium carbonate, and after agitation with ether to separate unaltered phenol, the solution is precipitated with hydrochloric acid. The phenolcarbonic acid when pure crystallises in needles having a nacreous lustre. It is only sparingly soluble in cold water, but very soluble in alcohol, ether, and chloroform. Its aqueous solution gives an intense blue-violet colour with ferric chloride. It melts at 98°, and distils without decomposition. Its *barium* salt, $(C_{10}H_{11}O_3)_2Ba + 3H_2O$, crystallises in colourless, micaceous scales. The *lead* salt, $(C_{10}H_{11}O_3)_2Pb + 2H_2O$, crystallises from boiling water in long plates. The *silver* salt, $C_{10}H_{11}O_3Ag$, is a white precipitate.

As in the process of preparing carbo-acids by the action of sodium and carbonic anhydride, the carboxyl usually occupies the ortho-position relatively to the OH group, it is highly probable that *parapropylphenolcarbonic* acid has the constitution $C_3H_7 : OH : COOH = [1 : 4 : 5]$.

β-propylphenol, obtained from the more soluble β-barium salt, is a colourless liquid, which boils at 224·6—226·6° (corr. to 0° and 758·5 mm.), and does not solidify in a mixture of ice and salt. Density at 0° = 1·0150, and at 99·8° = 0·93702. It is but very sparingly soluble in water. The *methyl ether* boils at 207—209° (corr. to 0° and 757·7 mm.), and has a density of 0·96944 at 0°, and 0·916772 at 99·88°. The oxidation of this compound with chromic mixture did not give a successful result; only a minute quantity of an acid being obtained, which began to melt at 100°, but was not completely fused

below 130°. The author thinks it probable, however, that β-propylphenol is an ortho-compound in which $C_3H_7 : OH = [1 : 2]$, as it differs entirely from the metapropylphenol (m. p. 26° : b. p. 228°) obtained by Jacobsen from camphothymol (*Ber.*, **11**, 1058).

Orthopropylphenolcarbonic acid crystallises in colourless needles (m. p. 93—94°), which cannot be distilled without decomposition. It dissolves readily in hot water, and is very soluble in alcohol, ether, and chloroform. Its *barium* salt, $(C_{10}H_{11}O_3)_2Ba + 2\frac{1}{2}H_2O$, crystallises to nodules consisting of pearly scales. The *lead* salt, $(C_{10}H_{11}O_3)_2Pb + 2H_2O$, is a crystalline precipitate. The *silver* salt, $C_{10}H_{11}O_3Ag$, is a white precipitate which blackens on exposure to the light. It is probable that the constitution of this acid is $C_3H_7 : OH : COOH = [1 : 2 : 3]$.

From the author's experiments it will be seen that propylbenzene boils 6° higher than cumene: that propylbenzene, when treated with sulphuric acid, yields two sulphonic acids, whilst cumene yields only one; and that the phenols obtained from the first two are liquid, whilst that from cumene-sulphonic acid is a solid, melting at 61°. Moreover, the carbo-acids derived from the liquid phenols both melt below 100°, but that from cumophenol at 120°; and lastly cumic acid differs from parapropylbenzoic acid. These considerations, together with the fact that when sodium acts on a mixture of bromobenzene and isopropyl iodide, cumene is generated, render it certain that cumene contains the isopropyl group, and that synthetical propylbenzene contains normal propyl in the side-chain. C. E. G.

Action of Fused Soda on Phenol. Synthesis of Phloroglucinol.—By L. Barth and J. Schreder (*Deut. Chem. Ges. Ber.*, **12**, 417—423). The chief products obtained on fusing phenol with soda are phloroglucinol, pyrocatechol, and resorcinol, which together form about 10—15 per cent. of the phenol used; other products are formed, but in very minute quantities. Phloroglucinol thus prepared is identical with that obtained from maclurin: the melting point of both preparations is 206° (uncorr.), and not 220° as usually stated. This action of caustic soda is entirely different from the action of caustic potash.

The authors have also prepared phloroglucinol synthetically from Senhofer's benzenetrisulphonic acid (*Wien. Acad. Ber.*, **78**, ii), who found that only two of the HSO_3 groups can be replaced by OH by fusion with potash; by the use of soda, however, the authors have been able to replace all three of the HSO_3 groups, and thus obtained phloroglucinol. By this synthesis, the aromatic nature of phloroglucinol is definitely established. P. P. B.

Oxidation of Resorcinol to Phloroglucinol. By L. Barth and J. Schreder (*Deut. Chem. Ges. Ber.*, **12**, 503—508).—Resorcinol was oxidised by fusion with soda, the fused mass was dissolved in dilute sulphuric acid, and the acid solution extracted with ether. On evaporating the ether, phloroglucinol crystallised out; the yield of this substance forming from 60 to 70 per cent. of the resorcinol taken. The mother-liquor from the phloroglucinol gave with lead acetate a yellow precipitate, which on decomposition by hydrogen sulphide, yielded a syrupy

liquid. This substance decomposed on distillation, forming pyrocatechol. The filtrate from the lead precipitate contained a small quantity of unaltered resorcinol, but it chiefly consisted of phloroglucinol and tetroxydiphenol $C_{12}H_{10}O_4$. The latter substance forms a crystalline powder or long, colourless needle-shaped crystals, which do not melt at 250°. It is much less soluble in water, and more soluble in ether than phloroglucinol. It gives with ferric chloride, a blue, and with concentrated sulphuric acid, a citron-yellow coloration.

W. C. W.

Phthalyl Alcohol. By J. Hessert (*Deut. Chem. Ges. Ber.*, **12**, 646—648).—The author has prepared the alcohol, $C_6H_4(CH_2.OH)_2$, by the action of sodium amalgam on phthalic chloride. It is a crystalline body, soluble in water, alcohol, and ether; it melts gradually at 56—62°.

It is oxidised by potassium permanganate to phthalic acid, by nitric acid to phthalide. It is distinguished from the latter compound, which it otherwise resembles, by the action of sulphuric acid; this reagent dissolves it with a red colour, and rapidly converts it into resinous products. On reduction, by boiling it with hydriodic acid and phosphorus, it yields orthoxylene. It reacts readily with acetic and benzoic chlorides; the acetate, $C_6H_4(CH_2.O\bar{A}c)_2$, is a crystalline body (m. p. 37°), which may be distilled without decomposition. By the action of hydrochloric acid gas, it is converted into the chloride $C_6H_4(CH_2Cl)_2$. This chloride was heated with lead nitrate and water, with the view to convert it into the unknown phthalic aldehyde, Grimaux having in this way obtained benzaldehyde from benzyl chloride (*Annalen*, **143**), but with negative results, phthalide being the chief product of the reaction. C. F. C.

Cholesterin. By K. Preis and B. Raymann (*Deut. Chem. Ges. Ber.*, **12**, 224—225). — When finely-powdered anhydrous cholesterin is dropped into cold, red fuming nitric acid, it fuses, and is converted into a dinitro-compound, which solidifies when washed with cold water. This has the composition $C_{26}H_{42}(NO_2)_2O$ or $C_{25}H_{40}(NO_2)_2O$; it is insoluble in ether, but crystallises from boiling alcohol in slender colourless needles (m. p. 120—121°).

Cholesteryl chloride similarly treated gives a mononitro-compound, $C_{26}H_{42}(NO_2)Cl$ or $C_{25}H_{40}(NO_2)Cl$, which crystallises from hot alcohol in colourless needles (m. p. 148—149°). Ch. B.

Specific Rotatory Power of Isocholesterin. By E. Schultz (*Deut. Chem. Ges. Ber.*, **12**, 249).—Isocholesterin, discovered some years ago by the author in wool-fat (*Ber.*, **6**, 251), differs from cholesterin in being *dextrorotatory*, whereas the latter is lævorotatory. Its specific rotatory power, when dissolved in ether, is $[\alpha]_D = +60°$, obtained by multiplying $n°$ (*Soleil-Ventzke*) by 0·346, and is independent of the concentration of the solution. Ch. B.

Orthocresolphthaleïn. By G. Fraude (*Deut. Chem. Ges. Ber.*, **12**, 237—244).—The phthaleïn of orthocresol, $C_6H_4[CO.C_6H_3(CH_3).OH]_2$, is prepared by heating a mixture of two parts orthocresol, three parts

phthalic anhydride, and two parts stannic chloride, at 120° for 8—10 hours. Unaltered cresol is removed from the product by superheated steam, and the phthaleïn is dissolved out from the residue by soda, precipitated with sulphuric acid, dissolved in alcohol, and decolorised by animal charcoal. When the alcoholic solution is filtered into a large quantity of water, it deposits flesh-red crystalline crusts of the new body (m. p. 213—214°). It dissolves easily in alcohol, ether, and acetic acid, but with difficulty in benzene. A *diacetyl* derivative, $C_6H_4[CO.C_6H_3(CH)_3.O\bar{A}c]_2$ (m. p. 73—75°), and a similar *dibenzoyl* derivative (m. p. 195—196°), may be obtained by boiling the phthaleïn with acetic anhydride and benzoic chloride respectively.

When an equal weight of bromine is gradually added to the phthaleïn, dissolved in ten parts of alcohol, *dibromo-orthocresolphthaleïn*, $C_{22}H_{16}Br_2O_4$, is formed (m. p. 255°). The alkaline solutions of this body are blue. If an excess of bromine (six parts dissolved in an equal weight of acetic acid) is added to the same alcoholic solution, one cresol group is separated from the phthaleïn as bromocresol, and the residue is oxidised to *monobrominated monorthocresolphthaleïn*, $C_6H_4(COOH).CO.C_6H_2Br(CH_3).OH$. The crystals which are deposited after some days are small and prismatic (m. p. 228°). The substance dissolves in dilute alkalis, and forms with barium a yellow, soluble, and crystallisable salt (Ba displacing both phenolic and acid hydrogen). Phosphoric chloride converts it into the crystalline chloride, $C_{15}H_{10}O_3BrCl$ (m. p. 208°). It belongs, therefore, to a class of bodies discovered by Baeyer, of which *monoresorcinol-phthaleïn*, $C_6H_4(COOH).CO.C_6H_3(OH)_2$, was the first representative (*Annalen*, **183**, 23).

The action of nitric acid on the phthaleïn, dissolved in 80—100 times its weight of concentrated sulphuric acid, gives rise to a dinitro-compound (m. p. 240°). The same compound is obtained with great ease by passing nitrous acid into an ethereal solution of the phthaleïn.

Derivatives of anthraquinone are obtained by the action of sulphuric acid on some of the above compounds. Thus, by the action of sulphuric acid on the phthaleïn, or by heating two parts cresol and three parts phthalic anhydride with 100 parts concentrated sulphuric acid at 160°, *methylhydroxyanthraquinone* is formed. This body sublimes in the form of brilliant golden-yellow plates. Similarly, *methylbromhydroxyanthraquinone* is obtained when either dibromo-orthocresolphthaleïn or monobromo-monorthocresolphthaleïn is heated with excess of strong oil of vitriol; and the same compound is formed when four parts dibromophthaleïn, one part phthalic anhydride, and 100 parts oil of vitriol, are heated at 150°; it melts at 205°. Both the anthraquinone derivatives are converted into *methylalizarin* by prolonged heating at 200° with potash. This substance is separated from the solution of the fused mass by hydrochloric acid, and purified by solution in ether and sublimation. It crystallises in brilliant orange-coloured needles (m. p. 250—252°). It has already been prepared by O. Fischer from methylanthraquinone (*Ber.*, **8**, 676).

By boiling an alkaline solution of the phthaleïn with zinc-dust, *orthocresolphthalin*, $C_{22}H_{20}O_4$, has been obtained; and dibromo- and diacetyl-derivatives of this compound are also described. Concentrated sulphuric acid converts it into *orthocresolphthalidin*, the solution

of which in ether or alcohol shows the characteristic green fluorescence of the phthalidins. Exposure to air oxidises this body to *orthocresolphthalideïn*, the smallest quantity of which communicates a deep violet colour to strong sulphuric acid.

Certain theoretical conclusions may be drawn from these experiments. The great resemblance between the methylalizarin described above, and alizarin, justifies the assumption that one is derived from the other: representing, with Baeyer, the constitution of alizarin by the scheme, $C_6H_4 : (CO)_2 : C_6H_2(OH)_2$ (in which OH : OH = 1 : 2), methylalizarin must have the constitution OH : OH : CH_3 = [1 : 2 : 3], since it is prepared from orthocresol. This view is in harmony with Nietzky's formula for the isomeric methylquinizarin (*Ber.*, **10**, 2014), which, being formed from phthalic anhydride and toluquinol, must have the constitution OH : CH_3 : OH = [1 : 3 : 4]. It necessarily follows, then, that methylhydroxyanthraquinone must have the constitution OH : CH_3 = [2 : 3], and its bromine derivative the constitution Br : OH : CH_3 = [1 : 2 : 3].

Again, since *methylhydroxyanthraquinone* is a derivative of ordinary hydroxyanthraquinone (as proved by the analogy between their chemical characters), the latter must have the constitution $C_6H_4 : (CO)_2 : C_6H_3(OH)$, in which OH = 2; and since the latter and its red isomeride (*erythrohydroxyanthraquinone*) may both be converted into alizarin, the red form must have the constitution OH = 1. This conclusion is confirmed by Liebermann's (*Ber.*, **10**, 611, and **11**, 1611) synthesis of erythrohydroxyanthraquine from hydroxyhydroanthranol—

$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>C_6H_3(OH), \text{ where } (OH = 1),$$

a reduction-product of quinizarin.

Finally, it is evident, especially in view of the easy conversion of monobromo-monorthocresolphthaleïn into methylbromhydroxyanthraquinone, that in the phthaleïn itself the side-chains of each cresol nucleus must have the arrangement, CO : OH : CH_3 = [1 : 3 : 4] or [1 : 4 : 3]. In its bromine derivative, bromine must be in the ortho-position with respect to hydroxyl. Ch. B.

Diphenylphthalide (Phthalophenone) and Phenolphthaleïn. By A. Baeyer (*Deut. Chem. Ges. Ber.*, **12**, 642—646).—*Constitution of "Phthalophenone."*—The equation by which Friedel and Crafts represented the formation of the compound, termed by them phthalophenone, viz.:—

$$C_6H_4(COCl)_2 + 2C_6H_6 = C_6H_4(CO.C_6H_5)_2 + 2HCl,$$

is shown by the author to be symmetrical at the expense of fact. What actually occurs is, the substitution of the O-atom of one of the COCl groups by $(C_6H_5)_2$; and the entire reaction occurring in two stages may be represented by the equations:—

$$C_6H_4(COCl)_2 + 2C_6H_6 = C_6H_4.C(C_6H_5)_2Cl.COCl + H_2O$$

$$C_6H_4<\begin{matrix}C(C_6H_5)_2Cl\\COCl\end{matrix} + H_2O = C_6H_4<\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}>O + 2HCl,$$

and is therefore analogous to the formation of phthalide:—

$$C_6H_4<\begin{matrix}COCl\\COCl\end{matrix} + 2H_2 = C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>O + 2HCl.$$

The proof of this view of the formation and constitution of "phthalophenone" lay in its conversion into the alcoholic acid, $C_6H_4(CPh_2.OH).COOH$, by boiling with alcoholic potash, and the reduction of the OH-group in this compound, whereby a stable acid was obtained which proved to be diphenylmethane-carbonic acid, $CHPh_2.C_6H_4.COOH$. The so-called phthalophenone is therefore diphenylphthalide.

Conversion of Diphenylphthalide into Phenolphthaleïn. — This was effected by nitration, reduction of the mixture of dinitro-compounds, and treatment of the larger fraction of isomeric bases (m. p. 179—180°) with potassium nitrite in acid solution. The stages of the conversion—

$C_{20}H_{14}O_2$, diphenylphthalide,
$C_{20}H_{12}(NH_2)_2O_2$, diamidophthalide,
$C_{20}H_{12}(OH)_2O_2$, phenylphthalin,

and the identification of the product, leave no doubt that phenolphthaleïn is a dihydroxydiphenylphthalide.

Constitution of Phenolphthaleïn.—The author then proceeds to show the harmony of the above view of its constitution with the known reactions of phenolphthaleïn.

(1.) As regards its formation. This occurs according to the equation—

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + 2(C_6H_5.OH) = C_6H_4<\begin{matrix}C(C_6H_4.OH)_2\\CO\end{matrix}>O + H_2O,$$

and is analogous to the action of the aldehyde on phenols in presence of dehydrating reagents:—

$$CH_3.COH + 2(C_6H_5.OH) = CH_3.CH(C_6H_4.OH)_2 + H_2O.$$

(2.) Its resolution into dioxybenzophenone and benzoic acid by fusion with potash, according to the equation—

$$(C_6H_4.OH)_2C<\begin{matrix}C_6H_4\\O\end{matrix}>CO + H_2O = CO(C_6H_4.OH)_2 + C_6H_5.COOH.$$

(3.) The action of phosphorus pentachloride yields the dichloride $(C_6H_4Cl)_2C<\begin{matrix}C_6H_4\\O\end{matrix}>CO$. Phthalin is a dioxytriphenylmethane-carbonic acid, $CH(C_6H_4.OH)_2.C_6H_4.COOH$, and phthalol the corresponding alcohol; phthalin gives in fact a di-, and phthalol a tri-acetyl compound.

The formation of phthalidin, on the assumption that a COOH-group attacks a $C_6H_4.OH$-group, as it attacks a C_6H_5 group in the formation of anthraquinone from benzoylbenzoic acid, will be represented by the equation—

$$C_6H_4<\begin{matrix}CH.C_6H_4.OH\\C_6H_4.OH\\COOH\end{matrix} = C_6H_4<\begin{matrix}CH.C_6H_4.OH\\CO\end{matrix}>C_6H_3.OH + H_2O,$$

the analogous reaction being—

$$C_6H_4<\begin{matrix}COC_6H_5\\COOH\end{matrix} = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + H_2O.$$

Phthalideïn will be OH. C. C_6H_4OH, related to phthalidin as tri-

$$C_6H_4<\begin{matrix}\\CO\end{matrix}>C_6H_3.OH$$

phenylcarbinol is to triphenylmethane.

(4.) The close relation of phenolphthaleïn to rosolic acid is evident from an inspection of the formulæ:—

$$(C_6H_4.OH)_2C<\underline{\begin{matrix}C_6H_4\\\end{matrix}}>O \quad \text{and} \quad (C_6H_4.OH)_2C<\underline{\begin{matrix}C_6H_4.CO\\\end{matrix}}>O.$$

Rosolic acid. Phenylphthaleïn.

C. F. C.

Synthesis of Oxyketones. By O. Doebner and W. Wolff (*Deut. Chem. Ges. Ber.*, **12**, 661—663).—This is a continuation of previously published researches (*Ber.*, **9**, 1918; **10**, 1968; **11**, 2268). The authors have prepared dibenzoquinone dibenzoate by heating quinol benzoate (m. p. 199°) with benzoic chloride and zinc or aluminium chloride at about 200°, the reaction being $C_6H_4(O\bar{B}z)_2 + 2\bar{B}zCl = \bar{B}z_2C_6H_2(O\bar{B}z)_2 + 2HCl$. This compound crystallises from its alcoholic solution in colourless plates (m. p. 146°). From this salt, *dibenzoquinol* is obtained by saponification. It crystallises in bright yellow needles (m. p. 207°), which are insoluble in water, easily soluble in hot alcohol. It is readily oxidised by ferric chloride and by silver nitrate in presence of ammonia.

The authors have not succeeded in preparing the monobenzoyl compound, isomeric with benzoresorcinol (*Ber.*, **11**, 2271); the capacity of forming mono- and di-substitution compounds of this class appearing to vary not only with temperature, but also with the position of the OH-group in the phenol. C. F. C.

Paratoluic and Terephthalic Acid. By H. Fischli (*Deut. Chem. Ges. Ber.*, **12**, 615—622).—According to the author, *paratoluic acid*, prepared from cymene, melts at 180° (after distillation) and not at 176—178° as usually stated, and boils at 274—275°.

Paratoluamide, $C_6H_4Me.CONH_2$, was obtained by Cahours, by the action of toluic chloride on ammonium carbonate (*Annalen*, **108**, 317), but he did not describe its properties. After repeated crystallisation from hot water, it is obtained in slender needles (m. p. 151°), freely soluble in alcohol and in ether. It forms a silver compound, which undergoes partial decomposition on solution in water.

Paratoluanilide, $C_6H_4Me.CONHPh$, prepared by the action of toluic chloride on aniline in ethereal solution, forms white plates (m. p. 139°).

Methyl paratoluate, $C_6H_4Me.COOMe$, is a crystalline compound, the product of the reaction of toluic chloride and methyl alcohol. It melts at 32° and boils at 217°. Its odour is powerful but very pleasant.

Sulphoparatoluic acid, $C_6H_3Me(SO_3H).COOH$, is formed by passing

the vapour of sulphuric anhydride over finely divided toluic acid. It crystallises in needles, which are easily soluble in water, soluble in alcohol, but insoluble in ether. When heated to 185—190° it is decomposed without previous fusion. It is remarkable that it does not deliquesce on exposure to the air. The properties of this acid are not such as to identify it with those obtained by Fleisch, Bechler, and by Fittica, by the oxidation of cymene mercaptans. The author describes the normal salts of lead, crystallising with 3 mols. H_2O, silver with 1 mol., barium with 3 mols., and of magnesium with 7 mols. H_2O.

Sulphoparatoluamide, $C_6H_3Me(SO_2.NH_2).CONH_2$, prepared by the action of ammonia on the corresponding chloride, crystallises in long needles, melting at 228°. When allowed to remain over sulphuric acid until its weight is constant, it still retains $\frac{1}{2}$ mol. H_2O, which, however, it loses at 160°.

Monobromoterephthalic acid, $C_6H_3Br(COOH)_2$, was prepared by the action of potassium permanganate on bromotoluic acid, in alkaline solution. It crystallises from its solution in boiling water or alcohol in microscopic needles (m. p. 304—305°). Contrary to the general relation of solubilities between the aromatic acids and their bromine derivatives, it is more readily taken up by solvents than terephthalic acid. It retains 1 mol. H_2O after drying at 120°.

The potassium salt crystallises in silky needles; the copper salt is obtained as a blue crystalline precipitate, the lead and silver salts as flocculent precipitates. The latter retains 1 mol. H_2O after drying at 120°.

By prolonged fusion with sodium hydrate, bromoterephthalic acid is decomposed according to the equation: $C_6H_3Br(COOH)_2 + 6NaOH = NaBr + 2Na_2CO_3 + C_6H_5.ONa + 3H_2O$. By adding the acid to the soda in the state of fusion, stirring for a short time, and then leaving the liquid to cool, the elimination of carbonic anhydride is prevented, and a large yield of hydroxyterephthalic acid free from bromine is obtained. The equation $C_6H_3Br(COOH)_2 + 3NaOH = NaBr + 2H_2O + C_6H_3(OH)(COONa)_2$, appears to be realised. The acid separates from its hot aqueous solution as a white crystalline powder, which does not melt at 330°. It is identical with Burkhardt's oxyterephthalic acid (*Ber.*, **10**, 144).

Bromoterephthalic chloride, $C_6H_3Br(COCl)_2$, is a colourless oily liquid, boiling at 305° without decomposition. It reacts with ammonia to form the corresponding amide, a body crystallising in colourless needles (m. p. 270°), which are not dissolved in the cold, by water, alcohol, or ether.

Methyl bromoterephthalate, $C_6H_3Br(COOMe)_2$, is formed by the action of the above chloride on methyl alcohol. It crystallises in needles which melt at 42°. Its boiling point is above 300°.

C. F. C.

Dinitrohydrocinnamic Acid and its Derivatives. By S. Gabriel and J. Zimmermann (*Deut. Chem. Ges. Ber.*, **12**, 600—603).—Glaser and Buchanan (*Zeits. Chem.*, 1869, 193) obtained a mixture of ortho- and para-mononitrohydrocinnamic acid by the action of cold nitric acid on hydrocinnamic acid.

Paradinitrohydrocinnamic (or *dinitrophenylpropionic acid*)—
$C_6H_3(NO_2)_2.C_2H_4.COOH$,
is formed when hydrocinnamic acid is slowly added to warm fuming nitric acid. On pouring the acid liquid into water, the nitro-product separates out after some time as a yellowish crystalline precipitate. It forms long needles or short thick prisms (m. p. 126·5°), which are soluble in alcohol, ether, acetic acid, and hot water. This acid forms a white crystalline silver salt, and an ethyl salt which crystallises in silky needles (m. p. 32°).

Amidonitrohydrocinnamic acid, $NO_2.NH_2.C_6H_3.C_2H_4.COOH$, prepared by the action of ammonium sulphide on the dinitro-product, forms red plates (m. p. 138°) soluble in water, ether, acetic acid, and warm alcohol.

Amidohydrocarbostyril, $NH_2.C_6H_3<\begin{matrix}NH\\C_2H_4\end{matrix}>CO$, is obtained in long colourless prisms (m. p. 211°), by reducing dinitrohydrocinnamic acid with tin and hydrochloric acid, and then adding an excess of soda to the mixture. This compound is soluble in boiling water, warm alcohol, and glacial acetic acid. It has no acid properties, but on the contrary it unites with acids to form crystalline compounds. On the addition of bromine to an acetic acid solution of amidohydrocarbostyril, a mixture of *mono-* and *di-*bromamidohydrocarbostyril is deposited. On recrystallisation from hot water, the dibromo-compound separates out in colourless flattened needles (m. p. 179°) soluble in chloroform. The momobromo-derivative is precipitated on the addition of soda to the mother-liquor. It crystallises in pale yellow needles (m. p. 219°), soluble in acetic acid and in alcohol. W. C. W.

Phenylcinnamic Acid. By A. Ogialoro (*Gazzetta chimica italiana*, **8**, 429—434).—This acid was prepared by Perkin's synthetical method (this Jour., 1877, i, 388) of forming acids. Sodium phenylacetate (25 grams) is heated with benzaldehyde (16 grams) and acetic anhydride (60 grams) at about 160° for 8 hours. The product boiled with water and filtered from the insoluble portion deposits nearly pure phenylcinnamic acid on cooling. The insoluble portion yields a further quantity of the acid when it is boiled with baryta-water, and the solution, after passing carbonic anhydride to remove excess of baryta, is precipitated with hydrochloric acid. Pure phenylcinnamic acid, $C_{15}H_{12}O_2$, crystallises in long slender needles (m. p. 169—170°). It is sparingly soluble in cold water, very soluble in alcohol and in ether. The *silver* salt, $C_{15}H_{11}O_2Ag$, and the *lead* salt $(C_{15}H_{11}O_2)_2Pb$, are both white precipitates. The *barium* salt $(C_{15}H_{11}O_2)_2Ba + 4H_2O$, crystallises in micaceous plates. The *ethyl* salt is liquid.

From the formula of cinnamic acid, $C_6H_5.CH:CH.COOH$, it is evident that various isomeric phenylcinnamic acids can exist, but the mode of formation from phenylacetic acid, $CH_2Ph.COOH$, and benzaldehyde, renders it probable that the phenylcinnamic acid just described has the formula $CHPh:CPh.COOH$, the reaction being $COH.Ph + CH_2Ph.COOH = CHPh:CPh.COOH + OH_2$. If this formula be the correct one for phenylcinnamic acid, it should be con-

verted by the action of nascent hydrogen into Wurtz' dibenzylcarbonic acid, $CH_2Ph.CHPh.COOH$ (*Compt. rend.*, **68**, 1298), and the author has proved that this actually takes place when the phenylcinnamic acid is treated with sodium amalgam and water. The author points out that the difference of 86° between the melting points of phenylcinnamic acid (170°) and Wurtz' dibenzylcarbonic acid (84°) is the same as that between cinnamic acid (133°) and hydrocinnamic acid (47°).

If the equation given above correctly represents the reaction, the function of acetic anhydride as a simple dehydrating agent, is quite different from that which it has in the experiments on the synthesis of cinnamic acid described by Perkins (*loc. cit.*). C. E. G.

Salicylates and their Application. By Vulpius (*Arch. Pharm.* [3], **14**, 239—245).—The difficulty with which metallic salts of salisalicylic acid dissolve in water, hinders their application both as disinfecting and as therapeutic agents. The zinc and copper salts, however, dissolve easily in alcohol, but this solvent is also at times a bar to their use. The atropine salt on the other hand is highly hygroscopic, and this property likewise renders it difficult to prepare a solution of known strength. It is, therefore, thought advisable to employ the sulphates of the metals, dissolved in a $\frac{1}{4}$ per cent. aqueous salicylic acid solution. E. W. P.

Ethereal Oils of some Ericaceæ. By H. Köhler (*Deut. Chem. Ges. Ber.*, **12**, 246—248).—The author has examined the oils of *Gaultheria punctata* and *G. leucocarpa*, and finds both to consist of nearly pure *methyl salicylate*. The first probably contains a little *gaultherilene*. The oils are thus almost identical with that of wintergreen (*G. procumbens*). Ch. B.

Hydroxyparaxylic Acid. By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **12**, 434—437).—By fusing pseudocumenol with potash, Reuter (*Ber.*, **11**, 30) obtained hydroxy-xylic acid, and since it yielded a liquid xylenol by distillation with lime, he attributes to it the constitution Me : Me : OH : COOH [1 : 3 : 4 : 6].

The author, however, finds that by heating this acid with hydrochloric acid at 220—225°, it is resolved into carbonic anhydride and a solid xylenol. This xylenol boils at 222—225°, melts at 61°, and forms a sulphonic derivative, the barium and sodium salts of which agree in their properties with those of orthoxylenolsulphonic acid (*Ber.*, **11**, 4).

The hydroxy-xylic acid, therefore, yields 1 : 2 : 4 orthoxylenol, and its constitution is consequently that of hydroxyparaxylic acid—

Me : Me : OH : COOH [1 : 2 : 4 : 5].

Hydroxyparaxylic acid is insoluble in cold, and but sparingly soluble in hot water; alcohol, ether, or chloroform dissolves it easily. From its hot aqueous or dilute alcoholic solutions, it crystallises in feathery needles, and from its concentrated alcoholic solutions in small compact prisms. It is volatile in aqueous vapour, melts at 199°, and sublimes

easily. Ferric chloride produces a violet-blue coloration in its solutions, and a violet precipitate in concentrated solutions of the sodium salt.

The barium salt forms small hard, anhydrous crystals, which are sparingly soluble in water. Solutions of the sodium salt produce crystalline precipitates in concentrated solutions of manganese, zinc, cadmium, and copper sulphate, also with lead nitrate and mercuric chloride. With silver nitrate, it yields a flocculent precipitate sparingly soluble in hot water, and crystallising from the hot solution in small rhombic plates united to stellate groups.

By continued fusion with potash, hydroxyparaxylic acid is converted into two dicarbonic acids, which are not volatilised by steam, and the solutions of which give a cherry-red coloration with ferric chloride. The author has found that the acid obtained by fusion of orthoxylenol with potash (*Ber.*, **11**, 381), and described by him as hydroxytoluic acid, is hydroxyparaxylic acid, and owes its existence to the presence of pseudocumene in the orthoxylenol employed. P. P. B.

Phenoxypropionic Acid. By L. Saarbach (*J. pr. Chem.* [2], **19**, 175—176).—The new acid, $CH_3.CH(OC_6H_5).COOH$, is formed by the action of sodium phenylate on α-chloropropionic acid; it crystallises from hot water in brilliant needles, which melt at 112—113°. By adding bromine-water to a hot aqueous solution of this acid, *monobromophenoxypropionic acid*, probably $CH_3.CH(OC_6H_4Br).COOH$, is produced. M. M. P. M.

Cumenolcarbonic Acid (Propylhydroxybenzoic Acid). By E. Paternò and G. Mazzara (*Gazzetta chimica italiana*, **8**, 389—391).—The cumenol employed in the experiments was prepared from cumic acid cumene by converting it into the sulphonic acid and fusing the potassium salt with potash: it was purified by distillation and then exposed in portions of 20 grams at 145—150° for eight hours to a current of carbonic anhydride, sodium being added from time to time. The product after exposure to the air, to oxidise the unattacked sodium, was treated with hydrochloric acid, and the mixture of unaltered cumenol with the new acid was washed with a solution of ammonium carbonate, which dissolved the latter. The cumenolcarbonic acid, $C_6H_3(C_3H_7)(OH).COOH$, thrown down from the ammoniacal solution by hydrochloric acid, and purified by crystallisation from dilute alcohol, forms flat needles, or iridescent plates (m. p. 120·5°). It is volatile without decomposition, sparingly soluble in cold water, very soluble in alcohol or ether. Its aqueous solution gives a very deep blue-violet coloration with ferric chloride. The *barium* salt, $(C_{10}H_{11}O_3)_2Ba$, crystallises in indistinct plates, which are unctuous to the touch, and acquire a rose tint on exposure to the air. The *lead* salt, $(C_{10}H_{11}O_3)_2Pb$, obtained by precipitating the barium salt with lead nitrate, is sparingly soluble in boiling water, and crystallises out on cooling in minute needles of a very pale rose colour. The *silver* salt, $C_{10}H_{11}O_3Ag$, prepared in a similar manner to the lead salt, closely resembles the latter.

The product of the action of phosphorus pentachloride on the acid, when treated with water, regenerates the original acid. It is evident that the cumenolcarbonic acid described by the authors is an isomeride

of the hydroxycumic acids hitherto obtained, as it is in all probability OH : C_3H_7 = [1 : 4], whilst the thymoloxycumic acid of Barth (*Ber.*, **11**, 567), and the isoxycumic acid of Jacobsen (*Ber.*, **11**, 1058), is OH : COOH = [1 : 4]. C. E. G.

Sulphaminemesitylenic Acids and a New Hydroxymesitylenic Acid. By O. Jacobsen (*Deut. Chem. Ges. Ber.*, **12**, 604—608).—The acid which Hall and Remsen (*Ber.*, **10**, 1040) obtained by the action of chromic acid on mesitylenesulphamide is not *para*- but *ortho*-sulphaminemesitylenic acid. A mixture of the ortho- and para-acids is formed by the oxidation of mesitylenesulphamide with potassium permanganate.

Orthosulphaminemesitylenic acid, $C_6H_2Me_2(SO_2.NH_2).COOH$, crystallises in anhydrous prisms, which melt at 263° (corr.); it is only sparingly soluble in hot water, but dissolves freely in alcohol and ether. The *barium* salt forms silky needles containing 3 mols. of H_2O. 100 parts of water at 0° dissolve 3·27, and at 20°, 14 parts of this salt. The *copper* salt crystallises in pale blue silky needles containing 3 mols. of H_2O. On fusion with potash, the ortho-acid yields mesitylenic acid, but with soda, a mixture of mesitylenic acid and metaxylenesulphamide [1 : 3 : 4], melting at 137°, is produced.

Parasulphaminemesitylenic acid is deposited from an aqueous solution in anhydrous needles (m. p. 276°). It dissolves freely in alcohol and ether, and is much more soluble in hot water than its isomeride. The *barium* salt forms long needle-shaped crystals containing 2 mols. of H_2O. 100 parts of water at 0° dissolve 2·05 parts. The *copper* salt crystallises in small monoclinic prisms of an ultramarine colour, containing 1 mol. of OH_2. It is sparingly soluble in hot water. When parasulphaminemesitylenic acid is fused with potash, *parahydroxymesitylenic acid* is formed. This acid is also obtained by adding potassium nitrite to β-amidomesitylenic acid dissolved in dilute sulphuric acid. It crystallises in colourless needles, soluble in alcohol and ether, which melt at 223°, and may be sublimed.

The *barium* salt crystallises in short anhydrous prisms which are freely soluble in hot water. *Methyl parahydroxymesitylenate* (m. p. 130°) and *ethyl parahydroxymesitylenate* (m. p. 113°) crystallise in needles.

Solid metaxylenol [1 : 2 : 3] is formed by heating parahydroxymesitylenic acid with strong hydrochloric acid at 200°. W. C. W.

Action of Nitrous Anhydride on Protocatechuic Acid. By M. Gruber (*Deut. Chem. Ges. Ber.*, **12**, 514—522).—When nitrous anhydride is passed into an ethereal solution of protocatechuic acid, nitric oxide and carbonic anhydride are evolved, and a complicated reaction takes place, 100 parts of protocatechuic acid yielding oxalic acid, 16·66; carboxytartronic acid, 10·50; dinitrodioxyquinone, 0·60; trinitrophenol, 4·0; α-dinitrophenol, 3·5; and nitrohydroxybenzoic acid, 1·00 part.

The ethereal solution was shaken with water, and both the ethereal and aqueous extracts examined separately. On the addition of sodium carbonate to the aqueous solution, sodium carboxytartronate separates

out as a heavy white crystalline powder. When the filtrate from this precipitate is neutralised with sodium carbonate, glistening yellow scales of sodium dinitrodioxyquinone are deposited. The mother-liquor contained oxalic acid and a nitro-product which could not be isolated.

Sodium carboxytartronate is decomposed by water (in which it is almost insoluble) at 60°, carbonic anhydride being given off and sodium tartronate formed,

$$OH.C(COONa)_2(COOH) = OH.C(COONa)_2H + CO_2.$$

The same change takes place when the dry sodium salt is heated at 100°. Carboxytartronic acid has not been isolated.

Sodium dinitrodioxyquinone, $C_6Na_2N_2O_8 + 2H_2O$, has a strong metallic lustre, and resembles brass in colour. It dissolves freely in hot water, forming a brown solution. The free acid is very unstable; it crystallises in long greenish-yellow needles, which are freely soluble in water or alcohol, and but sparingly in ether.

On evaporating the ethereal solution of the crude product of the action of nitrous anhydride on protocatechuic acid, a mixture of picric acid, α-dinitrophenol, and nitro-hydroxybenzoic acid is deposited. The mother-liquor contains picric and oxalic acids and a small quantity of a nitro-product which dissolves in potash with a splendid purple coloration.

The nitrohydroxybenzoic acid was separated from α-dinitrophenol by recrystallisation from cold alcohol, in which the latter is sparingly soluble. It was purified by recrystallisation from hot benzene. It is deposited from this solution on cooling, in compact yellow needles (m. p. 178°), which are freely soluble in alcohol, ether, and hot water. The hydrochloride of the amidohydroxybenzoic acid obtained by reduction of the nitro-acid with tin and hydrochloric acid, crystallises in slender needles. The sulphate forms microscopic crystals.

W. C. W.

Dioxybenzoic Acids. By L. Barth (*Wien. Akad. Ber.* [2], **77**, 769—772).—The substances $C_{12}H_{10}O_3$ and $C_{24}H_{18}O_5$, obtained from resorcinol by the action of hydrochloric or hydriodic acid under pressure, are also produced by distilling diethoxybenzoic acid with caustic lime, and heating the product with 5 or 6 vols. of fuming hydrochloric acid at 160—200°. The author enumerates reactions which show the identity of the substances prepared by the two methods.

M. M. P. M.

Nitrophthalic Acid obtained by Oxidation of Nitronaphthalene. By Beilstein and Kurbatoff (*Bull. Soc. Chim.* [2], **31**, 200).—Nitrophthalic acid melting at 135° is obtained by oxidising nitronaphthalene with chromic anhydride in acetic solution. Hydrobromic acid decomposes it into carbonic anhydride and di- and tribromobenzoic acids; hydriodic acid transforms it into metamidobenzoic acid.

J. M. H. M.

Phenylglyceric or Styceric Acid. By R. Anschütz and L. P. Kinnicutt (*Deut. Chem. Ges. Ber.*, **12**, 537—542).—The following compounds crystallise in the monoclinic system:—

Phenylmonobromopropionic acid, m. p. 137·5°, $a : b : c = 1·3613 : 1 : 1·5962$, $\beta = 69° 14'$.

Phenyldibromopropionic acid, m. p. 196°, $a : b : c = 0·23916 : 1 : 0·346933$, $\beta = 78° 38'$.

Methyl phenyldibromopropionate, m. p. 117°, $a : b : c = 0·930885 : 1 : 1·51683$, $\beta = 82° 38'$.

Ethyl phenyldibromopropionate, m. p. 69°, $a : b : c = 1·15761 : 1 : 1·62549$, $\beta = 88° 40'$.

Propyl phenyldibromopropionate, m. p. 23°.

Methyl dibenzoylphenylglycerate, m. p. 113·5°, $a : b : c = 0·96569 : 1 : 0·9008$, $\beta = 82° 14'$.

Ethyl dibenzoylphenylglycerate, m. p. 109°, $a : b : c = 1·9882 : 1 : 0·87261$, $\beta = 83° 4'$.

Methyl dibenzoylphenylglycerate is decomposed by the action of alcoholic potash, potassium benzoate and phenylglycerate being formed. After precipitating the benzoic acid with hydrochloric acid, the filtrate is evaporated to dryness, and the phenylglyceric acid is extracted from the residue by boiling ether.

Phenylglyceric acid melts at 117°, but it begins to decompose at 100°. It is soluble in water, alcohol, and to a small extent in ether. The potassium, barium, and silver salts are not crystalline.

The acid is converted into ethyl dibenzoylphenylglycerate by the following process. It is heated with benzoic chloride at 150° until the evolution of hydrochloric acid ceases; alcohol is then added to the liquid, and the mixture is saturated with hydrochloric acid gas, when the ethereal salt is deposited in crystals (m. p. 109°) which are identical in every respect with those obtained by the action of silver benzoate on ethyl phenyldibromopropionate. This shows that the acid bears the same relation to phenylglycerol or stycerin as glyceric acid does to glycerol. The authors accordingly name it phenylglyceric or styceric acid, and express its constitution by the formula

$$C_6H_5.CH(OH).CH(OH).COOH.$$ W. C. W.

Preparation of Digallic Acid. By P. Freda (*Gazzetta chimica italiana*, **8**, 363—371).—The author has repeated his attempts to prepare digallic acid from gallic acid by Schiff's method, and, as stated in a preliminary communication (*ibid.*, p. 9, and this Journal, 1878, Abst., 672), the product instead of being amorphous is always crystalline. He has now carefully examined the crystalline body, and finds it to consist of gallic acid. His former statement that it gave a precipitate with gelatin is incorrect, as he finds that it does not when free from every trace of arsenic. Not only has the author exactly followed Schiff's directions for the preparation of digallic acid, but he has also varied the conditions, using alcohol of different strengths and varying quantities of arsenic acid, but in every instance he has failed to obtain Schiff's digallic acid. As the crude product of the action of arsenic acid on gallic acid—before treatment with hydrogen sulphide—has many properties in common with tannic acid, the author adopted another method of purification. The alcoholic solution was evaporated to dryness, taken up with water, and the aqueous solution, after agitation with ether and concentration, was precipitated

with hydrochloric acid. The glutinous precipitate was then carefully washed with hydrochloric acid and finally with a little water. Its aqueous solution, like that of tannin, precipitates albumin, gelatin, and the alkaloïds. It gives a greenish-black precipitate with ferric salts, and is thrown down from its aqueous solutions in an amorphous state by mineral acids. It melts at 125—130°, and contains 8·49 per cent. arsenic. It would thus appear that by the action of arsenic acid on gallic acid, whether in aqueous or alcoholic solution, a substance is formed which gives many of the reactions of tannin. This substance, however, always contains arsenic, and as soon as the arsenic is removed it is completely changed into gallic acid. In conclusion the author remarks that if Schiff has actually converted gallic acid into the so-called digallic acid by the action of arsenic acid, he should indicate the precise conditions of its preparation and purification, that other chemists may repeat his experiments. C. E. G.

Digallic Acid. By H. Schiff (*Gazzetta chimica italiana*, **9**, 1—22).—After stating that Loewe had already obtained a tannic acid, which did not contain any appreciable quantity of glucose, by treating ordinary commercial tannin with ethyl acetate, and by the dialysis of an alcoholic solution of tannin previously treated with ether, the author describes a sample of tannin prepared by Schering, of Berlin, which only contained 2·7 per cent. glucose; other samples contained 3—4 per cent. The reactions of these preparations correspond exactly with those of the digallic acid obtained by the action of arsenic acid or phosphorus oxychloride on gallic acid. In his earlier papers on this subject, the author stated that the gallic acid was almost entirely converted into digallic acid by this treatment, but this he finds to be incorrect. The origin of the error is that gallic acid dissolves in large quantity in hot solutions of digallic acid, and on cooling, exhibits the phenomenon of supersaturation in a remarkable degree; sometimes the solution will remain for weeks without any gallic acid being deposited, and even when crystals of gallic acid are introduced, it frequently happens that days elapse before crystallisation sets in. On mixing such a supersaturated solution with a solution of common salt, the greater part of the gallic acid is thrown down along with the tannic acid: moreover, if arsenic acid is present and hydrogen sulphide is passed into the solution, the crystallisation of the gallic acid is induced by the arsenic sulphide which is precipitated. It would appear also that even after hydrogen sulphide has been passed into the arsenical solution for several hours, and the saturated solution has been allowed to stand for several days, the whole of the arsenic is not precipitated; this is probably due to the solubility of arsenic sulphide both in aqueous solution of hydrogen sulphide and also in solution of digallic acid. The author states that the gallic acid and dissolved arsenic sulphide may be separated by means of ether containing a certain quantity of alcohol, and that other well known methods then serve for the final purification of the crude digallic acid thus obtained. It still, however, contains traces of arsenic.

Neither arsenic acid, nor gallic acid, nor a mixture of the two gives the characteristic reactions of tannin, but these reactions are at once

obtained if the mixture is boiled for a few minutes. For instance, neither gallic acid nor a mixture of gallic with arsenic acid precipitates quinine sulphate, whilst an abundant precipitate is obtained with digallic acid, either natural or artificial, and that whether arsenic acid is present or not.

When the solution of artificial digallic acid, prepared by the action of arsenic acid, is precipitated with hydrogen sulphide, the precipitate of sulphur and arsenic sulphide contains gallic acid, which may be separated by boiling it with water. If arsenic acid be now added to the solution of digallic acid, a precipitate of arsenic sulphide is at once produced by the dissolved hydrogen sulphide, and on passing hydrogen sulphide the remainder of the arsenic is thrown down. This precipitate, like the first, contains gallic acid, and the solution of digallic acid remaining gives the tannin reactions in a less marked manner. By repeating the treatment with arsenic acid and hydrogen sulphide, it is found that the precipitated arsenic sulphide always contains gallic acid; whilst the tannin reaction of the digallic acid solution gradually becomes feebler. The gallic acid obtained from these precipitates retains a portion of the digallic acid, and its solution shows the phenomenon of supersaturation previously noticed: large, coloured crystals of gallic acid (m. p. 235—240°: triclinic octahedrons), and small almost colourless crystals are deposited side by side from this solution. The experiment just described renders it probable that digallic acid is decomposed by excess of arsenic acid, so that it is not advisable to greatly increase the quantity of the latter, 8·10 per cent. of the gallic acid being the most advantageous proportion. In time, a comparatively small quantity of arsenic acid can convert a relatively large quantity of gallic acid into digallic acid.

Digallic acid, like natural tannin, is removed even from its dilute aqueous solution by agitation with ethyl acetate.

In conclusion, the author criticises Freda's results (see p. 645), and insists that whether or not in the conversion of gallic into digallic acid an arsenical compound is formed as an intermediate product, the tannin reactions are quite independent of it. The precipitated sulphur and arsenic sulphide always contain gallic acid, derived in part from a particular decomposition of the digallic acid.

He also points out that ellagic acid prepared by the action of arsenic acid on gallic or digallic acids at 160°, obstinately retains traces of arsenic, but has all the properties of ellagic acid obtained by other methods. C. E. G.

Benzoic Cyanide and Phenylglyoxylic Acid. By L. Claisen (*Deut. Chem. Ges. Ber.*, **12**, 626—632).—This is a continuation of previously published researches (*Ber.*, **10**, 429; 844; 1663).

Benzoic cyanide crystallises from its solutions in long prisms of the regular system. Relation of the axes $a : b : c = 2{\cdot}6565 : 1 : 2{\cdot}8403$; $\beta = 60° 51'$. It dissolves in sulphuric acid to a yellowish liquid, which on standing deposits benzoic acid. If gently warmed, a more rapid decomposition ensues, with evolution of a gaseous mixture of carbonic oxide and anhydride (3 vols. CO : 1 vol. CO_2).

By the action of phosphorus pentachloride, it is converted into a

chloride, $C_8H_5Cl_2N$, which appears to be phenyl dichloracetonitril, $C_6H_5.CCl_2.CN$. It is a colourless liquid, boiling at 223—224° without decomposition.

Phenylglyoxylic Acid.—The salts of this acid are well characterised compounds, soluble in water. The potassium salt, $C_8H_5O_3K + H_2O$, crystallises from its aqueous solution in large four-sided plates; from its solution in hot alcohol, in slender prisms. The sodium salt is deposited from its aqueous solution in small prisms, which are soluble in cold alcohol. The ammonium salt crystallises in large plates, which are easily soluble in alcohol.

The calcium salt, $(C_8H_5O_3)_2Ca.H_2O$, forms tufts of needles; it is only slowly dehydrated at 100°. The barium salt, $(C_8H_5O_3)_2Ba$, crystallises in prisms which are insoluble in alcohol. The silver salt is a crystalline precipitate. The copper salt is anhydrous; it melts at 160—170° to a dark-green liquid.

Ethereal salts of this acid are easily prepared by passing hydrochloric acid gas into alcoholic solutions of benzoic cyanide kept well cooled by means of a freezing mixture. The methyl and ethyl salts may be distilled without decomposition under the ordinary pressure, the higher homologues only under diminished pressure. The following are their boiling points:—

	Boiling point.	Pressure.
Ph.CO.COOMe	246—248°	760 mm.
Ph.CO.COOEt	256—257	760 „
Ph.CO.COOPr$^{\alpha}$	174	60 „
Ph.CO.COO.CH$_2$.Pr$^{\beta}$	170—174	38 „
Ph.CO.COO.(CH$_2$)$_2$Pr$^{\alpha}$....	179—182	40 „

The methyl, ethyl, and isobutyl salts, when brought in contact with a concentrated solution of hydrogen-sodium sulphite, solidify to crystalline masses of the respective double compounds. The propyl and amyl phenyloxalates are dissolved by the solution, and the corresponding compounds are deposited in well-formed crystals on allowing the solution to stand. Advantage is taken of this property for preparing the ethereal salts in the pure state. By the action of phosphorus pentachloride on the ethyl salt, ethyl phenyldichloracetate is formed, according to the equation $Ph.CO.COOEt + PCl_5 = Ph.CCl_2.COOEt + POCl_3$. It is a pleasantly smelling dense liquid, boiling at 263—266°. The corresponding acid is a deliquescent crystalline body, easily soluble in water, alcohol, and ether.

The following properties of phenylglyoxylic acid are also described. Its aqueous solution undergoes no change on prolonged boiling. By the action of warm concentrated sulphuric acid, it is resolved into benzoic acid and carbonic oxide; the same decomposition occurs, although less completely, on heating it with concentrated hydrochloric acid at 150°. It is only slowly acted on by boiling dilute nitric acid, and by potassium permanganate in alkaline solution. On subjecting the silver salt to dry distillation, a crystalline product is obtained, containing, in addition to benzoic acid, an oily body, which however does not appear to be benzil, as was supposed by Zincke (*Ber.*, **10**, 1489). C. F. C.

Amides of Phenylglyoxylic Acid. By L. Claisen (*Deut. Chem. Ges. Ber.*, **12**, 632—636).—This is supplementary to a previous communication (*Ber.*, **10**, 1663), in which the author had described as isomerides, three amido-compounds, α, β, and γ, obtained from benzoic cyanide. The β-compound, which was obtained as a crystalline precipitate, on passing carbonic anhydride into a solution of the α-amide in cold dilute potash, has been since proved to be a hydrate of the latter, $C_8H_5O_2.NH_2.H_2O$, which readily loses its water at 50—60°, as well as on standing over sulphuric acid. The previous analyses having been made with a preparation which had remained for some time over sulphuric acid, were performed upon the α-amide itself: hence the mistake as to its being an isomeric body.

It is worthy of note that this hydrate crystallises unchanged from its solution in warm water, but that if the solution is boiled, the amide crystallises in the anhydrous state. A similar result is obtained on dissolving the hydrate in alcohol and allowing it to crystallise.

The α-amide is converted quantitatively into the γ-compound on pouring its alcoholic solution, drop by drop, into excess of cold dilute hydrochloric acid. It is a white powder, insoluble in water and in ether; it is somewhat soluble in alcohol, and crystallises from this solution in small prisms.

On boiling with water, it is reconverted into the α-modification. A similar conversion takes place on heating it to its melting point, 134—135° (on allowing it to cool and then again heating, the substance melts at 80—90°). The author regards it as holding a polymeric relation to the α-amide, its probable constitution being expressed by the formula $Ph.(CONH_2)C:O_2:C(CONH_2)Ph$.

In conclusion, the author states that he has in no case obtained evidence of the existence of the supposed isomeride of phenylglyoxylic acid described by Hübner (*Ber.*, **10**, 479). C. F. C.

Sulphonic Acids derived from Sulphones. By R. Otto (*Deut. Chem. Ges. Ber.*, **12**, 214).—When sulphobenzide and sulphuric monochloride, in molecular proportion, are heated at 120°, hydrochloric acid is given off and *sulphobenzid-monosulphonic acid*,

$$C_6H_5.SO_2.C_6H_4.HSO_3,$$

is formed (*Ber.*, **11**, 2075). Under similar conditions, but using twice the quantity of sulphuric chloride, *sulphobenzid-disulphonic acid*, $C_{12}H_8(HSO_3)_2SO_2$, is obtained with facility. The barium salt of this acid crystallises easily from hot water, and has the composition $C_{12}H_8[(SO_2.O)_2Ba]SO_2 + 5H_2O$.

The author could not obtain a trisulphonic acid. Ch. B.

Fluobenzenesulphonic Acid, and on the Melting Points of Substituted Benzenesulphone Derivatives. By W. Lenz (*Deut. Chem. Ges. Ber.*, **12**, 580—583).—The substance which the author formerly regarded as a compound of hydrofluoric acid with the di-azo-derivative of sulphanilic acid (*Ber.*, **10**, 1135), is merely a mixture of the two acids.

Parafluobenzenesulphochloride, $C_6H_4(Fl)(SO_2Cl) = [1:4]$, crystal-

lises in colourless rhombic plates or needles (m. p. 36°), having a peculiar odour. It is soluble in ether, chloroform, and benzene.

Parafluobenzesulphamide, $C_6H_4Fl.SO_2NH_2$, is deposited from an aqueous solution in colourless rhombic plates or long needles (m. p. 123°), which are freely soluble in ether, alcohol, and acetone.

In the para-series the melting points of the substituted chlorides and amides of benzenesulphonic acid rise as the molecular weight of the compound increases; but no relation between the melting point and molecular weight has been observed in the ortho- and meta-series.

Chlorides.

	Fl.	Cl.	Br.	I.
Para ..	36°	53°	75°	86—87°
Meta ..	—	liquid	liquid	—
Ortho..	—	28·5	51	51

Amides.

Para ..	123	143—144	160—161 (Goslich) / 166 (Nölting)	183
Meta ..	—	148	153—154	—
Ortho..	—	188	186	170

W. C. W.

Formula of Hipparaffin. By H. Schwarz (*Wien. Akad. Ber.*, **77**, ii, 762—768).—Hipparaffin is obtained by the action of lead peroxide on hippuric acid in presence of excess of sulphuric or nitric acid. It crystallises in small, brilliant needles, which are with difficulty attacked by any reagents: hence the name.

In a former communication (*Annalen*, **75**, 195) the author assigned the formula C_8H_8NO to hipparaffin. Maier (*Annalen*, **127**, 161) supposed that C_8H_7NO better expressed the composition of the compound, and he also described a new compound, *hipparin*, to which he assigned the formula $C_8H_9NO_2$.

In the present communication the author shows reason for doubting Maier's formula for hipparaffin, and also for believing that Maier's hipparin is none other than ethyl hippurate.

Detailed directions are given for the preparation of hipparaffin. When heated in sealed tubes with water, or better with dilute hydrochloric acid or soda solution, hipparaffin splits up into benzamide and one of the polymerides of ethaldehyde. By heating together benzamide and ethaldehyde, in presence of phosphoric anhydride, the author succeeded in preparing hipparaffin. There is some difference in its properties, however, compared with those of the hipparaffin prepared from hippuric acid, for not only is it more easily decomposed by acids, but it melts at 185°, whilst the melting point of the compound obtained from hippuric acid is 215°. These results show that the formula of hipparaffin must be doubled, so that it becomes $C_{16}H_{16}N_2O_2$; the rational formula is probably $C_2H_4(C_7H_6NO)_2$. M. M. P. M.

Sulphine Compounds of Thiocarbamide. By A. Bernthsen and H. Klinger (*Deut. Chem. Ges. Ber.*, **12**, 574—576).—By gently

warming a mixture of benzyl chloride and thiocarbamide, a crystalline compound, soluble in water and alcohol, is obtained, which melts at 167°, and has the composition $C_8H_{11}N_2SCl$. The free base, $C_8H_{10}N_2S$, is precipitated on adding ammonia or soda to a solution of the preceding compound. It is freely soluble in alcohol, ether, and in dilute acids, but is decomposed when boiled with water or benzene. The base melts at 71°, but soon decomposes, forming benzyl mercaptan and dicyandiamide. W. C. W.

Diphenylthiohydantoïn. By A. Lange (*Deut. Chem. Ges. Ber.*, **12**, 595—599).—On heating an alcoholic solution of diphenylthiocarbamide with monochloracetic acid, *diphenylthiohydantoïn*, $C_{15}H_{12}N_2SO$, separates out in iridescent plates (m. p. 176°), whilst the mother-liquor contains a compound having the composition $C_9H_7NSO_2$.

Diphenylthiohydantoïn is soluble in hot alcohol and in acids, but is reprecipitated on addition of water.

With platinum chloride, the hydrochloric acid solution yields a double salt, which crystallises in yellow prisms, and is decomposed by water.

When diphenylthiohydantoïn is boiled with alcoholic potash, it yields diphenylcarbamide. Dilute hydrochloric acid slowly converts it into the compound $C_9H_7NSO_2$, which is also obtained as a by-product in the preparation of the diphenylthiohydantoïn. It forms needle-shaped crystals, which are soluble in alcohol, benzene, ether, chloroform, carbon bisulphide, alkalis, acids, and in hot water. It melts at 148°, but begins to sublime below 100°.

By the action of potassium monochloracetate on diphenylthiocarbamide, a mixture of diphenylthiohydantoïn and diphenylthiohydantoic acid, $C_{15}H_{14}N_2SO_2$, is produced. The acid crystallises in pale yellow octahedra. W. C. W.

Action of Nitrous Acid on Stannic Phenyl Chloride. By B. Aronheim (*Deut. Chem. Ges. Ber.*, **12**, 509—510).—When sodium nitrite is added to an acetic acid solution of stannic diphenyl dichloride 85 per cent. of the compound is converted into stannic triphenyl chloride, nitrosobenzene being also formed.

(1.) $3Sn(C_6H_5)_2Cl_2 = 2Sn(C_6H_5)_3Cl + SnCl_4$.

(2.) $Sn(C_6H_5)_2Cl_2 + N_2O_3 = 2C_6H_5.NO + SnOCl$.

W. C. W.

Diphenols. By H. Schmidt and G. Schultz (*Deut. Chem. Ges. Ber.*, **12**, 490—498).—Besides the α- and β-diphenols of Barth and Schreder (*Ber.*, **9**, 1332), only two dihydroxybenzenes exist, viz.:—

(1.) γ-Diphenol (m. p. 272°), obtained either by the action of nitrous acid on benzidine (Griess, *J. pr. Chem.*, **101**, 92), or by fusing potassium diphenyldisulphonate with potash (Engelhardt and Latschinoff, *Ber.*, **6**, 194), or by distilling dioxyphenylbenzoic acid with lime.

(2.) δ-Diphenol (m. p. 161°, b. p. 342°), obtained either by treating γ-diamidodiphenyl with nitrous acid, or by fusing an alkaline paraphenolsulphonate with caustic alkali.

γ-Diphenol crystallises in brilliant plates or groups of needles, easily soluble in alcohol and ether. It is dissolved by alkalis, and thrown

down again on addition of an acid. It gives a pale green colour to concentrated sulphuric acid, but the presence of a trace of nitrogen peroxide changes it to blue. Ferric chloride has no action in the cold; but on heating, a brown precipitate is thrown down. Chloride of lime produces a fine but transient violet colour. Heated with acetic acid, it is converted into an acetyl compound (m. p. 159—160°), which dissolves in alkalis and reproduces the diphenol.

δ-Diphenol yields with acetic acid an acetyl compound (m. p. 94°), and is reduced by distillation with zinc-dust to diphenyl. It is identical with Lincke's diphenol obtained by fusing paraphenolsulphonic acid with potash (*Ber.*, **11**, 1339). G. T. A.

Diphenyl Bases. By H. Schmidt and G. Schultz (*Deut. Chem. Ges. Ber.*, **12**, 486—490).—The object of this paper is to show that when hydrazobenzene is treated with hydrochloric acid, there is formed in addition to benzidene and aniline, a new isomeric base, to which the authors have given the name of *δ-diamidodiphenyl*. Azobenzene in alcoholic solution is mixed with acid stannous chloride (prepared from a weighed quantity of the metal) and heated for a long time on the water-bath, using an upright condenser. The alcohol is distilled off, and the residue mixed with sulphuric acid and filtered from the separated benzidene sulphate. The liquid is then freed from tin by hydrochloric acid, mixed with ammonia and filtered. The filtrate, after concentration, is mixed with soda and treated with ether, and the residue left on evaporation of the ethereal solution is separated by fractional distillation into aniline and δ-diamidodiphenyl boiling at 363°. This body is not an intermediate product between hydrazobenzene and benzidine. The points of difference between the isomeric benzidine and δ-diamidodiphenyl are as follows.

The former dissolves easily in water, the latter with difficulty: the former yields large fine crystals, which melt at 122°, are tolerably stable and volatile at far over 360°; the crystals of the latter consist of long needles melting at 45°, unstable and difficult to obtain in a state of purity. Benzidine sulphate is almost insoluble, the sulphate of its isomeride is easily soluble. Benzidine chloride, $C_{12}H_{12}N_2.2HCl$, is easily soluble, and forms a platinum double salt with platinum chloride, but an excess of water converts it into $C_{12}H_{12}N_2.HCl$. The chloride of δ-diamidodiphenyl is easily soluble, but can only be crystallised by leaving the aqueous solution for a week mixed with a large excess of fuming hydrochloric acid; it gives no precipitate with platinum chloride.

Benzidine when treated with glacial acetic acid yields diacetylbenzidine (m. p. 317°), and the mother-liquor contains monacetylbenzidine, a body having basic properties. The diacetyl compound of δ-diamodiphenyl melts at 202°. When benzidine nitrate is saturated with nitrous acid and mixed with alcohol and ether, Griess' tetrazodiphenyl (*J. pr. Chem.*, **101**, 91) is obtained. This body treated with hydriodic acid yields a crystalline di-iododiphenyl melting at 202°, and which on oxidation is converted into pariodobenzoic acid. When it is mixed with an alcoholic solution of benzidine, a brown precipitate is obtained, which explodes when lighted. This latter body is also

formed by the action of nitrous acid on an alcoholic solution of benzidine, and is a compound of the diphenyl series analogous to diazoamidobenzene. An alkaline solution of phenol yields a brown precipitate on addition of hydrochloric acid, which dyes silk a fine pure yellow.

When the nitrate of tetrazodiphenyl from benzidine is converted into the sulphate and the solution of the latter is boiled with water, the diphenol (m. p. 272°) of Griess prepared in the same way and obtained by Engelhardt and others from diphenyldisulphonic acid is formed; but on the other hand, δ-diamidodiphenyl sulphate treated with nitrous acid and mixed with alcohol and ether, yields a brown oil, which, when boiled with water, is converted into the diphenol (m. p. 161°) obtained by Lincke from phenolparasulphonic acid. G. T. A.

Constitution of Phenanthrene. By G Schultz (*Deut. Chem. Ges. Ber.*, **12**, 235—237).—In a former paper (*Ber.*, **11**, 215) it was shown that diamidodiphenic acid obtained by Griess from metanitrobenzoic acid could be converted into diphenic acid, by first transforming it into diiododiphenic acid by the successive actions of nitrous and hydriodic acids, and then reducing the iodo-derivative with sodium amalgam. This diphenic acid has since been obtained in the pure state by dissolving the crude product in acetic anhydride, boiling the diphenic anhydride which separates on standing with dilute soda solution, and precipitating with sulphuric acid. Its melting point as thus prepared is 228—229°, which is also that of diphenic acid from phenanthraquinone (not 226° as previously given). Griess's acid is therefore *dimetamidodiphenic* acid.

Struve (*Ber.*, **10**, 75) states that by reducing dinitrodiphenic acid with tin and hydrochloric acid, he obtained an uncrystallisable isomeride of the above diamidodiphenic acid, which melted at 250—251°, and yielded by distillation with lime a diamidodiphenyl melting at 155—157°; whereas Griess's acid begins to melt at 170°, and when distilled with baryta, gives benzidine (dipara-amidodiphenyl). The author, however, shows that the two acids are identical: for both begin to melt at 170°, but are not completely liquefied at 270°; both may be obtained, either crystalline or amorphous; both, when treated with nitrous and hydriodic acids, yield the same diiododiphenic acid (m. p. 262°); and both, in the form either of salt or of hydrochloride, give by distillation with lime or baryta, either caustic or anhydrous, identical products, viz., *benzidine*, and a base melting at 157°. The latter is not, however, a diamidodiphenyl, but *diamidofluorene*. By treatment with nitrous acid, it yields fluorene.

The production of benzidine shows that diamidodiphenic acid is *diparamido-diorthocarboxyldiphenyl*, and phenanthrene, *diortho-diphenylene-acetylene*. Ch. B.

Anthrol. By C. Liebermann and O. Hörmann (*Deut. Chem. Ges. Ber.*, **12**, 589—592).—*Sodium anthracenesulphonate*, $C_{14}H_9.SO_3Na + 4H_2O$, is formed by the action of phosphorus and hydriodic acid on sodium anthraquinonemonosulphonate for a short time. The sodium, potassium, and ammonium anthracenesulphonates are colourless crystalline salts, sparingly soluble in water. The lead and barium salts are insoluble.

Anthrol, $C_{14}H_9OH$, is prepared by fusing sodium anthracenesulphonate with potash, dissolving the fused mass in water, and acidifying with an acid. The precipitated anthrol may be obtained in colourless plates by recrystallisation from acetone. It dissolves in baryta-water, or solution of potash or soda, forming a yellow liquid, which has a green fluorescence. The alcoholic solution reduces silver nitrate.

By heating soda with a mixture of ethyl iodide and anthrol at 120°, *ethyl anthrol ether*, $C_{14}H_9OEt$, is obtained as a red resinous mass. On recrystallisation from dilute alcohol, it is deposited in colourless needles (m. p. 139—140°).

Monacetyloxyanthraquinone, $C_{14}H_7O_2O\bar{A}c$, is deposited in colourless needles (m. p. 159°), when an aqueous solution of chromic acid is added to a hot solution of acetylanthrol in acetic acid. By boiling with potash, it is converted into hydroxyanthraquinone, $C_{14}H_7O_2.OH$.

The *α-* and *β-anthrol* and *anthracenesulphonic acids* described by Lincke (*J. pr. Chem.*, **11**, 225) do not agree in their properties with the preceding compounds. W. C. W.

α- and β-Nitroalizarin and β-Amidoalizarin. By E. Schunck and H. Roemer (*Deut. Chem. Ges. Ber.*, **12**, 583—589).—When nitric acid is added to alizarin suspended in acetic acid, a thick yellow deposit of *β*-mononitroalizarin, $C_{14}H_7(NO_2)O_4$, is obtained. The crude product is purified by solution in warm dilute potash, and the potassium derivative, which is deposited from the liquid on cooling, is decomposed by hydrochloric acid. After recrystallisation from glacial acetic acid, the *β*-mononitroalizarin is obtained in yellow plates, soluble in alcohol, chloroform, and benzene. It melts at 244°, with decomposition. This substance is identical with the compound which Rosenstiehl obtained by the action of nitrous acid on alizarin, and it is also the chief constituent of alizarin orange.

The *potassium* and *sodium* derivatives dissolve in water, forming purple solutions, which exhibit two absorption bands. The *barium* and *calcium* derivatives are brownish-red and insoluble. An alcoholic solution of lead acetate produces a red precipitate, and alcoholic copper acetate gives a red coloration. It colours an alumina mordant orange, and iron mordant reddish-violet.

The *α-mononitroalizarin* described by Perkin melts at 194—196°, and is more soluble in potash, but less soluble in alcohol and acetic acid than the *β*-modification.

The *barium* derivative is bluish-violet, and the *calcium* reddish-violet. Alcoholic solutions of lead and copper acetates produce red colorations.

A third isomeride is known which melts at 282°, but resembles *α*-nitroalizarin in its properties.

The *diacetyl* derivative of *β-nitroalizarin*, $C_{14}H_5(NO_2)O_2(O\bar{A}c)_2$, is deposited from a solution in benzene in long yellow needles (m. p. 218°). This compound appears to undergo partial decomposition when recrystallised from alcohol or acetic acid. *β-amidoalizarin* is formed by the action of reducing agents on the nitroalizarin. The best yield is obtained by passing sulphuretted hydrogen through a solution of the nitroalizarin in dilute ammonia. When the red precipitate

which separates out is recrystallised from glacial acetic acid, it yields the amidoalizarin in red prisms, melting above 300° and subliming with partial decomposition. This compound dissolves sparingly in alcohol, freely in sulphuric acid, forming a yellow, and in potash, forming a blue solution. It colours alumina mordants dull red, and iron dull grey. W. C. W.

Alizarinsulphonic Acid. By C. Graebe (*Deut. Chem. Ges. Ber.*, **12**, 571—574).—Von Perger's alizarinsulphonic acid (*J. pr. Chem.*, **18**, 173) is identical with the acid which the author and Liebermann obtained from a bye-product in the manufacture of alizarin, having the composition $C_{14}H_7O_4(SO_3Na) + H_2O$.

The acid forms three series of salts; the potassium and sodium salts are soluble in water; the salts of the alkaline earths and lead are sparingly soluble.

The salts, $C_{14}H_5O_2(OH)_2SO_3M'$, are orange or yellow in colour, and yield alizarin when heated. The salts, $C_{14}H_{15}O_2(OH)(OM').SO_3M'$ and $C_{14}H_{15}O_2(OM')_2.SO_3M$, do not give alizarin when heated. They have a violet or reddish-yellow colour. W. C. W.

Derivatives of Cantharidin and their relation to the Ortho Series. By J. Piccard (*Deut. Chem. Ges. Ber.*, **12**, 577—580).—A compound crystallising in slender needles (m. p. 131°), of the composition, $C_{10}H_{12}I_2O_3$, is formed by the action of hydriodic acid on cantharidin. It is soluble in benzene and chloroform, and crystallises therefrom in prisms belonging to the anorthic system. It is insoluble in a cold solution of potash. Pure cantharene, C_8H_{12} (b. p. 134°), obtained by heating the hydriodic acid derivative with a solution of potash in sealed tubes, possesses the property of absorbing 150 times its volume of oxygen. By oxidation with nitric acid, the hydrocarbon yields orthotoluic and phthalic acids.

When a solution of cantharidin in caustic soda is evaporated to dryness and the residue heated with soda lime, a mixture of cantharene, xylene, and high-boiling ketones distils over.

Orthoxylene (b. p. 141°) can be obtained in quantity by distilling cantharidin with phosphorus pentasulphide. W. C. W.

Cinchonine. By M. Fileti (*Deut. Chem. Ges. Ber.*, **12**, 423—425).—When a solution of cinchonine in hydrochloric acid is saturated with chlorine, a compound separates out which has probably the composition $C_{19}H_{20}N_2OCl_6 + HCl$. It is insoluble in the more ordinary solvents, but soluble in glacial acetic acid. If cinchonine is heated with bromine and water in sealed tubes at 150°, carbonic anhydride, ammonium bromide, and perbromethane are formed together with a yellow crystalline compound. The latter is sparingly soluble in the ordinary solvents, but dissolves in hot chloroform, and crystallises out again on cooling. In order to purify it, it is repeatedly sublimed in a current of carbonic anhydride, and thus obtained in yellow shining plates. From the analytical results, the author infers that this compound is perbromanthracene, $C_{14}Br_{10}$. P. P. B.

Conquinine Sulphate. By O. Hesse (*Deut. Chem. Ges. Ber.*, **12**, 425—426).—The author stated in a former communication (*Ber.*, **11**, 1166) that the green fluorescence observed by Schaer in a solution of quinidine sulphate, which has been kept for some time, was not due to conquinine sulphate, but to cinchonidine sulphate. He now finds, however, that a solution of conquinine sulphate in chloroform does become fluorescent after a time. P. P. B.

Oxidation-products of Cinchona Bases. By H. Skraup (*Deut. Chem. Ges. Ber.*, **12**, 230—234).—The author confirms the statements of Koenigs (*Ber.*, **12**, 97) with regard to cinchonic acid, its preparation, and constitution. He likewise has found that its true formula is $C_{10}H_7NO_2$, and not $C_{20}H_{14}N_2O_4$ as proposed by Weidel; and that it is chinoline-monocarbonic acid. To the description of it given by Koenigs, he adds that it melts at 256°, and that, when its solution in hydrochloric acid is evaporated to a small bulk, crystals of a hydrochloride are deposited, which decompose during the process of drying in a vacuum, giving off hydrochloric acid.

Weidel based his formula for cinchonic acid on the observation that it yielded by oxidation *chinolic acid*, $C_9H_6N_2O_4$, and *cinchomeronic acid*, $C_{11}H_8N_2O_6$. The author, however, doubts the correctness of the second of these formulæ, and thinks that Weidel's cinchomeronic acid will prove to be a dicarbopyridenic acid, $C_7H_5NO_4$. Caventou and Willm's *carboxycinchonic acid* is, he finds, simply cinchonic acid.

Cinchonic acid is produced by the oxidation with chromic mixture of cinchonine and cinchonidine, $C_{19}H_{22}N_2O$, and of cinchotenine and cinchotenidine, $C_{18}H_{20}N_2O_3$; but in the case of the latter two there is no evolution of carbonic anhydride. This is readily explained. Potassium permanganate converts cinchonine and cinchonidine into cinchotenine and cinchotenidine respectively, formic acid being given off. When dichromate is used as the oxidising agent, the same change occurs in the first instance; but the formic acid is further oxidised to carbonic acid, and the bases cinchotenine and cinchotenidine to cinchonic acid. Other volatile acids are produced from all four bases.

By oxidation with dichromate, quinine and conquinine also yield non-volatile acids, which differ from cinchonic acid. These have not yet been examined. Ch. B.

Berberine. By H. Weidel (*Deut. Chem. Ges. Ber.*, **12**, 410—417).—Fleitmann (*Annalen*, **59**, 160) found that oxalic acid is a product of the oxidation of berberine by nitric acid. The author finds, however, that no oxalic acid, but an acid containing nitrogen, is formed, which is styled *berberonic acid*. To prepare this acid, berberine is heated with eight to ten times its weight of nitric acid, the resulting solution is concentrated, and on cooling a crystalline mass separates out. The acid is further purified by crystallisation from hot water and conversion into the calcium salt, which separates from the hot aqueous solution as a crystalline precipitate. The filtrate from the calcium salt has a yellow colour, and contains the salt of an acid which forms an insoluble silver salt: from this, the acid may be ob-

tained in woolly needles. It has not been further investigated, as it occurs in very small quantities only.

Berberonic acid, obtained by decomposing the calcium salt with an acid and crystallisation from hot water, forms groups of shining, transparent, prismatic crystals, which become opaque on exposure to the air. It is sparingly soluble in cold, but easily in hot water; alcohol dissolves it but sparingly, and it is insoluble in ether, benzene, and chloroform. It has an acid taste, decomposes carbonates, and is decomposed by heat. When crystallised from dilute aqueous solutions, it forms triclinic prisms, having the composition $C_8H_6NO_6 + 2H_2O$, which on exposure to air lose one molecule of water and become opaque. Like oxycinchomeronic (*Wien Acad. Ber.*, 1874, *October heft*) and pyridendicarbonic acids (Ramsay, *Phil. Mag.*, 1877, 246), the aqueous solutions of berberonic acid give an intense red coloration with ferrous sulphate in absence of a stronger acid.

Calcium berberonate, $(C_8H_2NO_6)_2Ca_3 + 4H_2O$, is prepared by treating the ammoniacal solution of the acid with calcium chloride. It separates out in white shining needles, which after one crystallisation are insoluble in water.

The *cadmium* salt, $(C_8H_2NO_6)_2Cd_3 + 2H_2O$, crystallises in shining branching needles, and is sparingly soluble in water.

The *silver* salt, $C_8H_2NO_6Ag_3$, is obtained as a white crystalline precipitate.

When the calcium salt is distilled with lime, pyridine is obtained, together with other products, the decomposition taking place thus: $C_8H_5NO_6 = 3CO_2 + C_5H_5N$. When the acid is fused with potash, ammonia and hydrogen are evolved, and potassium cyanide and acetate are formed.

Berberonic acid may be regarded as pyridene-tricarbonic acid. In its reaction with ferrous sulphate, it resembles pyridene-dicarbonic acid (Devar, *Zeits. Chem.*, 1870). In this latter respect it also resembles oxycinchomeronic acid, to which it closely approximates in percentage composition. A comparison of the two acids has yielded the following results:—

	Oxycinchomeronic.	Berberonic.
Crystalline form.....	Prismatic.	Triclinic.
Water of crystallisation	10·84 per cent.; does not effloresce.	14·57 per cent.; effloresces quickly.
Calcium salt.....	Cauliflower-like crusts; 25·3 per cent. water.	Fine, flexible needles; 21·1 per cent. water.
Cadmium salt.....	White, crystalline powder; 12·2 per cent. water.	Needles having a satiny lustre; 8·73 per cent. water.
	Precipitated by copper acetate in the cold.	Precipitated only when hot, the precipitate redissolving on cooling.

P. P. B.

Alkaloïds of the Pomegranate. By C. Tanret (*Compt. rend.*, **88**, 716—719).—In the bark of the pomegranate, besides pelletierine,

there are three other volatile alkaloïds, which may be separated in the following manner. The powdered bark is mixed with milk of lime and treated with water; the solution is shaken with chloroform, which in its turn is shaken with a dilute acid. A solution containing a mixture of the alkaloïds is thus obtained, which is dextrogyrate, lævogyrate, or inactive, according to the bark used. To separate these alkaloïds, the solution is treated with sodium bicarbonate and saturated with carbonic anhydride; it is then shaken with chloroform, and the latter with dilute sulphuric acid. This solution, which is dextrogyrate, contains the sulphate of a dextrogyrate liquid alkaloïd and of an inactive solid alkaloïd.

By treating the solution in a similar manner, but using caustic soda instead of sodium bicarbonate, a lævogyrate solution is obtained, which after evaporation *in vacuo* over sulphuric acid leaves a crystalline sulphate of a lævogyrate liquid base, and an uncrystallisable sulphate of an inactive base. These may be separated by filtration. The active sulphate possesses the rotatory power $[\alpha]_j = -30°$.

Crystalline Base.—By decomposing with an alkali the dextrogyrate solution described above, treating with chloroform, and evaporating off the latter, crystals are obtained, which may be purified by recrystallisation. From an aqueous solution, prismatic crystals are deposited, having the formula $C_9H_{15}NO + 4H_2O$. It forms a double salt with platinum chloride, $(C_9H_{15}NO.HCl)_2 + PtCl_4$, crystallising in reddish-yellow needles. The hydrated base melts at 46°, but can be cooled to 37° without solidifying. It boils at 246°, and is soluble in alcohol, ether (9 parts at 10°), water (2·5 at 10°), and chloroform, which extracts it from its aqueous solution. It is a powerful base, expelling ammonia from its salts, and precipitating alumina, baryta, and lime, but not magnesia. It gives all the characteristic reactions for the alkaloïds, and with sulphuric acid and potassium dichromate gives, like pelletierine, an intense green colour.

The *hydrochloride*, $C_9H_{15}NO.HCl$, crystallises in rhombohedrons, and is soluble in its own weight of water at 10° C.

The *sulphate*, $C_9H_{15}NO.HSO_4.4H_2O$, crystallises with 4 mols. of water, which it loses over sulphuric acid. At 10°, it is soluble in less than twice its weight of water.

The author reserves naming this base until he has examined the other two. L. T. O'S.

A New Alkaloïd. By A. Petit (*J. Pharm. Chem.* [4], **29**, 18—20).—The author describes a white bitter root, whose origin and name are at present unknown to him. Its starch-granules are much smaller than those of wheat. It contains much saccharine matter, nine-tenths of which has no reducing action. When coarsely powdered and extracted with alcohol at a temperature of 80°, it yields an extremely bitter solution. The alcohol was distilled, the residue taken up with water, and the filtered liquid mixed with potassium bicarbonate and chloroform. Several treatments with chloroform were necessary to remove the bitter principle entirely; the chloroform solution was strongly alkaline. A syrupy residue remained on distilling the chloroform, and this crystallised the next day in tufts of fine needles and

very long prisms. A trace of colour was removed by treatment with well-washed animal charcoal. The body shows all the properties of the best defined alkaloïds, neutralising the strongest acids, and yielding precipitates even in dilute solution with the double iodides of potassium and mercury, with the double iodides of potassium and cadmium, and with gold chloride. No particular colorations are obtained by the reactions for strychnine and for quinine. The alkaloïd is characterised by its extreme bitterness, its great solubility in water, its inactivity towards polarised light, and by the solubility of its platinochloride. Other reactions are stated. Its physiological action was inappreciable when tested by hypodermic injection on frogs.

F. C.

Products of the Fermentation of Albuminoïds. By E. and H. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 648—653).—The decomposition of the several proteïds investigated by the authors, viz., wool, serum, albumin, blood and muscle fibrin, and fresh muscle, was effected by digesting them at 40°, for periods of 3—60 days, with a dilute solution of sodium carbonate (15 c.c. of the saturated solution diluted with 1,000 c.c. of water to 50 grams of the dry substance). In certain cases, pancreatic juice was added, in others, a few drops of a decomposing fluid containing *Bacillus subtilis*. On the completion of the decomposition, the solutions were distilled, and the distillate and residue separately treated for the isolation of the products.

Blood and muscle fibrin, and fresh muscle, all yielded phenylpropionic acid, in quantity about 0·5 per cent. of the dry substance, the duration of the digestion varying from 3 to 13 days. In one instance, in which fresh muscle was digested for 14 days, this acid was not formed, but a small quantity of phenylacetic acid was isolated.

Commercial serum albumin (125 grams) after digestion for 37 days also yielded phenylacetic acid (3 grams). The same acid was obtained from wool, in quantity about 0·6 per cent., and in addition an aromatic acid, $C_8H_8O_3$ (m. p. 148°), differing, however, in its properties from the known isomerides of this formula. It is probably one of the unknown oxyphenylacetic acids.

The early stages of the decomposition of muscle were attended by the formation of succinic acid, the maximum quantity observed being 1 per cent. of the dry substance. It is probably preceded by that of aspartic acid.

Muscle which had been previously treated in a dry, finely-divided state with boiling ether, yielded by decomposition a quantity of the higher fatty acids (3 per cent.); so also serum albumin.

In the further investigation of the products of decomposition of muscle, the following bodies were isolated from the distillate:—

Before the boiling point was reached, a small quantity of a heavy yellowish oil distilled. This proved to be a non-nitrogenous sulphur compound.

From the succeeding portions phenol, indole, and skatole (*Ber.*, **10**, 1027) were isolated. The occurrence of the latter body, however, was not constant. The quantity of indole obtained is remarkable; in one case 100 grams of dry substance yielded 0·9 gram of pure indole.

C. F. C.

Chemical Nature of Peptone. By R. Herth (*Wien. Akad. Ber.* [ii], **76**, 869—890).—Peptone was prepared by digesting the finely powdered white of egg from 50 to 60 boiled eggs for 24 to 30 hours with a 1 per cent. solution of phosphoric acid, then treating with hot water, and digesting with 4 litres of a 0·65 per cent. solution of phosphoric acid and 40 c.c. of a clear pepsin solution which had been purified by dialysis, and was free from calcium and chlorine. When the liquid had become clear (after 5 or 6 hours) it was heated on a sand-bath, and freshly precipitated lead carbonate was added to neutral reaction. The small quantity of lead present in the filtrate was removed by means of sulphuretted hydrogen; the liquid was again filtered, concentrated on the water-bath, precipitated, and digested with concentrated alcohol, again dissolved, and the liquid re-precipitated. This process was repeated three times. The precipitated lead phosphate was quite white, showing the absence of sulphide. A concentrated solution of the peptone thus prepared gave a slight turbidity with potassium ferrocyanide and acetic acid. Various methods of purification were employed, but the reaction with ferrocyanide was invariably obtained. Whether this reaction is due to a trace of unchanged albumin in the peptone, is regarded by the author as a yet unsettled point.

In the original paper a number of analyses of the peptone are given, both of the substance prepared as described above and of the various precipitates obtained by fractionally precipitating with alcohol and with lead acetate and ammonia. These analyses show that peptone is not a mixture, but a distinct chemical compound. The percentage composition of peptone appears to be identical with that of albumin obtained from egg white. The author regards albumin as a polymeride of peptone, and the change brought about by the action of pepsin solution in albumin as analogous to the action of heat in effecting the change of paraldehyde into vapour of aldehyde.

A solution of peptone is not precipitated by many of the salts of heavy metals, by acids, or by boiling. Alcohol, mercuric chloride, and lead acetate, followed by ammonia, cause precipitates in solutions of peptone. The statement of Adamkiewicz (*Die Natur und Nährwerth des Peptons*, Berlin, 1877) that those reagents which precipitate egg albumin also precipitate peptone is regarded by the author as incorrect. Peptone forms compounds with metals analogous to those formed by albumin, but the compounds of peptone are generally soluble, whilst those of albumin are insoluble.

The author claims for his process of preparing peptone that it ensures a complete or almost complete conversion of the albumin into peptone, that it entirely removes syntonin, and that the absence of salts of the alkaline earths is also ensured. These salts are very difficult to remove from solutions of peptone.

The amount of ash in the peptone prepared by the author's process is not more than 1 per cent. M. M. P. M.

Diastase and Beet Mucilage. By C. Zulkowsky (*Wein. Akad. Ber.*, **77** [ii], 647—654).—The preparation of diastase from malt is described in detail. Briefly the method consists in extracting malt

which has been freed from the shoots with strong alcohol, adding glycerol to the residue until a syrupy mass is obtained, removing air-bubbles by placing the whole under the receiver of an air-pump, filtering after 8 to 12 days through muslin and pressing, diluting the liquid with water, and again filtering into a mixture of absolute alcohol and ether. The diastase which is precipitated by the alcohol-ether mixture is washed with absolute alcohol until the last traces of glycerol are removed, and is then dried *in vacuo* over sulphuric acid.

Diastase as thus prepared is partly soluble in cold water; the solution quickly converts starch into glucose at a temperature of 40°. The mean of several analyses of diastase gave the following results:—

C.	H.	N.	Ash.	O and S.
47·57	6·49	5·14	3·16	37·64 = 100·00.

The ash contains phosphates of potassium, calcium, and magnesium, and small quantities of sulphates.

A substance resembling diastase has been obtained from beets by a process analogous to that described above. The examination of this substance is as yet very incomplete. M. M. P. M.

Chondrin. By R. Petri (*Deut. Chem. Ges. Ber.*, **12**, 267—269).—The nature of the reducing substance described by Bödecker, Meissner, and de Bary, as being formed when chondrin is acted on by acids, alkalis, or gastric juice, or undergoes putrefaction, is still unknown. It was at one time regarded as a species of sugar, and hence named "chondroglucose;" but von Mering, in 1873 (*Inaug. Diss.*), disproved this view, and pointed out its compound nature.

This substance is most easily formed when pure chondrin (from the tracheal cartilages of young bullocks) is heated with water containing at most 1 per cent. of sulphuric acid by injecting steam. All the chondrin having been decomposed, the opalescent viscous liquid is treated with barium carbonate, whereby sulphuric acid and syntonin are precipitated, and saturated with mercuric chloride to remove peptones. Alcohol precipitates the required substance from the filtrate; it is dissolved in water, and any mercury present removed by hydrogen sulphide. After repeated solutions and precipitations by alcohol, it is obtained colourless and free from albumin and peptones. Prolonged standing under alcohol renders it anhydrous and transparent, and by subsequent exposure to air it becomes crystallised, partly in rhombic tables, partly in fine needles.

The aqueous solution of this substance is very viscous, has a strongly acid reaction and is lævorotatory. It is precipitated by gold chloride and by lead acetate; but not by platinic chloride, tannin, mercuric or silver salts. Its presence prevents the precipitation of the two last by alkalis; but on warming such alkaline solutions, reduction and deposition of metal take place.

When a boiling solution of the substance is treated with pure basic copper carbonate, a dirty blue-green precipitate and a very soluble crystallisable copper salt are formed. The precipitate is soluble in both acids and alkalis. The alkaline solutions of both compounds deposit cuprous oxide on boiling. Ch. B.

Physiological Chemistry.

Distribution of Phosphates in the Blood. By L. Jolly (*Compt. rend.*, **88**, 756—759).—The author has determined the quantity of phosphates in the proteïds of the blood, which he divides into four groups :—(1) Aqueous part, (2) albumin, (3) fibrin, (4) globules; his results with ox blood are :—

Composition of the Blood.	Elements.	Phosphate				Total Phosphates.	Oxide of Iron not Phosphate.
		Alkaline.	of Calcium.	of Magnesium.	of Iron.		
809	Water	0·235	0·006	—	0·012	0·253	0·020
67	Albumin (dry)	0·032	0·027	—	0·189	0·248	—
3	Fibrin „	trace	0·015	0·004	0·016	0·035	—
121	Globules „	0·063	0·037	—	1·354	1·454	—
1,000		0·330	0·085	0·004	1·571	1·990	0·020

From this it is seen that the alkaline phosphates predominate in the liquid portion, and the phosphate of iron, although it varies in the different elements, seems to accumulate in the globules.

L. T. O'S.

Physiological Relations of Phenylacetic and Phenylpropionic Acids. By E. and H. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 653—655).—*Phenylpropionic* acid, given to a dog together with his food in quantities of 1·5—2 grams daily, was entirely converted, by oxidation, into benzoic acid, the urine containing hippuric acid, but no trace of homologous compounds. The authors having previously shown that phenylpropionic acid is an early product of the decomposition of proteïds by digestion and fermentation, this observation affords a simple explanation of the excretion of hippuric acid by the carnivora. The excretion of hippuric acid and of indican from the organism during starvation, points to a similar decomposition of tissue-proteïds.

Phenylacetic acid was converted under similar conditions into phenaceturic acid, $C_{10}H_{11}NO_3$, a crystalline body (m.p. 143°) resembling hippuric acid. On boiling with hydrochloric acid, it is easily resolved into phenylacetic acid and glycocine, its constitution is therefore expressed by the formula, $C_6H_5.CH_2.CO.NH.CH_2.COOH$. The remarkable difference thus observed between the physiological relations of these homologous acids, points to the limited applicability of Graebe's conclusion respecting the oxidation of the side chains of aromatic acids, to carboxyl, in the animal organism.

C. F. C.

"Starch Granules" and "Amyloids" of the Egg. By Dastre (*Compt. rend.*, **88**, 752—753).—The globules in the vitellus of eggs

do not consist of starch, but of a fatty body which appears to belong to the lecithines. They are seen in the new laid egg. The granules called "amyloides" by Dareste, do not, as the name implies, consist of starch, since they are not coloured blue by iodine or converted into glucose by diastase. They are not optically active. L. T. O'S.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Carbonic Anhydride, Alcohol, and Acetic Acid by Yeast alone, in Presence and Absence of Oxygen. By A. Béchamp (*Compt. rend.*, **88**, 719—721).—Yeast mixed with two or three times its weight of water was boiled, cooled in a current of carbonic anhydride to expel air, and the liquid maintained at a temperature of 25—30°. A regular current of carbonic anhydride was evolved throughout the experiment, and at the end nitrogen.

Alcohol and acetic acid were also formed in the proportion of 3·7 c.c. and 0·163 gram respectively, for 100 grams of dry yeast.

Yeast coated with creasote was kept at the temperature of the climate of Montpellier for two months, at the end of which time the percentage of alcohol and acetic acid for dry yeast was 10·8 c.c. and 1·5 gram respectively.

Under the influence of the electric current, yeast when mixed with water still continues to evolve carbonic anhydride, and alcohol and acetic acid are formed. Amongst the gases evolved is nitrogen, and the oxygen due to the decomposition of the water is rapidly absorbed.

In one experiment, the percentage of alcohol and acetic acid for dry yeast was 1·06 and 0·63 respectively; and in another 2·76 and 1·42, the percentage of organic and mineral matter being in the first case 27·5, and in the second 11·9. L. T. O'S.

Fermentation. By J. Schiel (*Deut. Chem. Ges. Ber.*, **12**, 508).—When a galvanic current is passed through a solution of sugar and ammonium phosphate, to which meat extract and yeast have been added, the formation of bacteria is prevented without interfering with the process of fermentation. W. C. W.

Conditions of Lactic Fermentation. By C. Richet (*Compt. rend.*, **88**, 750—751).—Lactic fermentation is greatly increased by exposing a large surface of the milk to the action of the air. Up to 44° the activity of the fermentation increases with the temperature, and remains constant between 44° and 52°. Above 52° the activity diminishes as the temperature rises; this appears to be due to the coagulation, by the heat, of some albuminoïd substance, which assists in the fermentation.

Digestive juices, such as the gastric juice, the pancreatic juice, and

peptones, increase the activity of the lactic fermentation; but nitrogenous bodies such as leucine, glycocoll, &c., have no action.

L. T. O'S.

Schizomycetic Fermentations. By A. Fitz (*Deut. Chem. Ges. Ber.*, **12**, 474—478).—This is a continuation of former papers (see this Journal, 1878, Abst., 241).

The first experiment was made with grams of *calcium glycerate*, which was mixed with cow-dung. A trace of alcohol, 24·5 grams of the calcium salt of a volatile acid, and a trace of a non-volatile liquid acid were obtained. The volatile acid was acetic, mixed with a trace of butyric acid; a small quantity of formic acid was also found. At the beginning of the fermentation, the liquid contained elongated cells of a micrococcus, which were often strung together in chains; towards the end, a round micrococcus was more abundant. The same cells were formed in the second experiment made with the same bodies. The products were ethyl alcohol, acetic acid, with a trace of a higher acid and formic acid. Water in which hay had been steeped but not boiled, was next tried, and the same schizomyces appeared together with a pear-shaped one, which was coloured violet by iodine. Products: ethyl alcohol, acetic acid with a trace of a higher acid, succinic acid.

Erythrol (erythrite) mixed with hay-water yielded a trace of alcohol, also butyric, acetic, and a trace of formic acid. The quantity of succinic acid was much less than in a former experiment, and it is probable that erythrol decomposes in two different ways, one yielding chiefly succinic acid, the other chiefly volatile acids.

Calcium tartrate and cow-dung.—In the liquid were found a long and a round micrococcus, and towards the end a bacillus and a bacterium, but the schizomyces of Pasteur could not be perceived. Products: ethyl alcohol acids; chiefly acetic with a little butyric, and a trace of formic and succinic. The author shows that the butyracetic acid of Nicklès (*Annalen*, **61**, 343) has no existence.

The fermentation products of *calcium lactate* were a trace of alcohol, propionic and acetic acids, and a small quantity of a volatile acid, probably undecomposed lactic acid.

Gelatin and albumin.—The former yielded no alcohol; the latter doubtful traces. The author considers that the reducing action attributed to the so-called *fermentation hydrogen* is due to a peculiar form of schizomycetes.

Calcium malate yields a little ethyl alcohol, acetic, succinic, and carbonic acids. Glycerol with the same schizomyces yielded alcohol, boiling at 78—80°; formic acid and another volatile acid unnamed; a little succinic acid.

G. T. A.

Conditions of Life of the Lower Organisms. By J. W. Gunning (*Chem. Centr.* [3], 1878, 799—800).—Tyndall has shown that in putrefaction, the presence of a limited quantity of air is necessary, otherwise it is totally arrested. Bacteria, in the presence of excess of oxygen, however, assume a death-like condition, from which they are aroused only by the presence of albumin or albuminoïds. This probably explains why atmospheric dust originates bacterial life in all

sterilised infusions of vegetable or animal substances, but not in solutions which are artificially prepared for the nourishment of bacteria by dissolving ammonium salts and sugar or tartaric acid: bacteria taken from putrefying liquids thrive in such solutions, but atmospheric germs refuse to develop. Bastian argues from this that atmospheric air contains no bacteria germs, but that bacteria are generated from albumin and albuminoïds. The author believes, however, that the action of oxygen in excess destroys albuminoïd matters which are necessary to the growth of bacteria; and this he confirms by showing that paper dipped into dilute putrefying liquid and dried slowly in the air, will not originate bacterial life in the artificially prepared solution, but does fertilise organic solutions which supply the necessary albuminoïds. An exactly parallel case is furnished by yeast, which has had its albuminoïds removed by repeated extraction with glycerol, or by allowing it to ferment as long as it will in excess of sugar solution: such yeast refuses to invert or ferment artificially made solutions of sugar, and appears dead, but its activity is restored by adding albuminoïds or by dropping in some of the glycerol extract obtained from the yeast. Further, just as the paper moistened with putrefying liquids and dried in the air was incapable of fertilising liquids free from albuminoïds, so yeast by exposure to excess of oxygen becomes apparently dead. The author deduces from this that germs may be prevented from developing by exposure to excess of oxygen, probably because certain albuminous and albuminoïd matters necessary to their development are separated by oxygen; this is probable since the activity is at once restored by addition of albuminous substances. Possibly these substances are only unorganised ferments, and the inverting substance separated from yeast therefore has its influence also in producing fermentation. F. C.

Phosphorescence of Lobsters' Flesh. By C. Bancel and C. Husson (*Compt. rend.*, **88**, 191).—A microscopic examination of lobsters' flesh, when phosphorescence appeared, showed the presence of reddish-yellow cells, which the authors regard as acting like plants, during the daytime, in fixing carbon and liberating oxygen, which last remains dissolved in the liquid, while the germ continued to live evolving carburetted hydrogen and phosphuretted hydrogen from the surrounding material, and these products are oxidised as they form, producing the phosphorescence. R. R.

Supposed Existence of Hydrogen Peroxide in the Organism of Plants. By G. Bellucci (*Gazzetta chimica italiana*, **8**, 392—406). Clermont, on treating the sap of plants with Schonbein's reagent (potassium iodide, starch and ferrous sulphate), obtained a blue coloration which he attributed to the presence of hydrogen peroxide in the juices. The author repeated Clermont's experiments with various species of plants, and found that in some cases he obtained the blue coloration, whilst in others he did not; further experiment showed that the blue colour was due merely to the action of the ferrous salt on the tannin present in those plants. The mere fact, therefore, of a blue

coloration being produced with Schonbein's reagent, is not conclusive evidence of the presence of hydrogen peroxide in plants.

In order to obtain positive proof of the absence of hydrogen peroxide, the author employed the test suggested by Barreswil, namely, the production of a blue colour on addition of a solution of chromic acid, and subsequent agitation with ether. The expressed sap was agitated with thrice its volume of ether, to remove chlorophyll, &c., and the clear or slightly opalescent aqueous layer was then agitated with a fresh portion of ether, after the addition of a small quantity of a 1 per cent. solution of chromic acid. In no instance was the blue colour characteristic of hydrogen peroxide obtained. It seemed, however, possible that the latter might have been removed or decomposed by the treatment to which the juice was subjected; experiments were therefore made with sap to which hydrogen peroxide had been added, but it could always be detected, sometimes even when the mixture had been allowed to stand for a day or more. These results exclude the possibility of the existence of hydrogen peroxide in the sap of plants. C. E. G.

Assimilation of Soda by Plants. By Dehérain (*Chem. Centr.*, 1878, 783—784).—Beans grown in water containing sodium chloride alone in solution assimilated the salt in small quantities, but if other salts were present in the water, sodium chloride was taken up only when its proportion was large compared with that of the other salts. The other salts employed were calcium and potassium nitrates. Beans grown in water containing 1 gram of each of the three salts, showed no trace of sodium in their ashes; if, however, the proportion of sodium chloride was raised to 4 grams, a small quantity was assimilated. In such a solution the plants lived several days, whereas in one which contained 4 grams of sodium chloride only, the assimilation of that salt was rapid, but the plants very soon died. The author finds that soda is taken up from the ground by beans only when its proportion to the other salts is large, and hence the absence of soda in the ash of the plant does not necessarily prove that the soil in which it was grown was free from soda, but may arise from the soda being mixed with sufficient quantities of other salts.

The laws of diffusion offer no explanation of the fact that sodium chloride is more readily assimilated in the absence of other salts. The author finds that when beans which had begun to germinate were placed in salt water, they frequently removed more salt than water; Böhn had shown that distilled water cannot support their growth, but that water containing calcium salts readily does so: hence the author concludes that the germinating beans assimilate by preference calcium and potassium salts, and take up sodium chloride only when the calcium and potassium salts are absent or are deficient in quantity relatively to the sodium chloride. F. C.

Constancy and Variation in the Composition of the Soil. By A. Orth (*Landw. Versuchs.-Stat.*, **23**, 388—389).—This is a concluding paper to the one already published (this Journal, 1878, Abst., 1003). The author now reviews the results of analyses of diluvial and

alluvial soils (from the environs of Berlin), which bear out his previously expressed opinion as to the importance of appreciating the changes which occur in the land profile or surface layer in its relation to geographical and practical questions. A. J. C.

Evaporation of Water from the Ground. By F. Haberlandt (*Chem. Centr.*, 1878, 830).—Glass cylinders of similar dimensions were filled with cultivated soil, sand, and "bog-earth" respectively; they were moistened with varying percentages of water, and their loss in weight by evaporation compared with that undergone by a similar cylinder of water at the expiration of four and of 24 hours. It was found that the evaporation increased with the percentage of water added, that it was augmented remarkably by rise in temperature of the air, and that moist sand and soil lost more by evaporation than the water itself. The rate of evaporation rapidly diminished if the loss of water was not made good. In comparison with the water given off by transpiration of plants, the evaporation from the surface of the soil is very great. It is evident from the above results that although repeated light showers will not penetrate to the roots of plants, the same quantity of rain falling in one shower may do so. The loss by evaporation was much lessened when salt water was substituted for fresh in moistening the soil. F. C.

Absorptive Powers of Soils. By F. Ullik (*Landw. Versuchs.-Stat.*, **23**, 347—372).—The author has investigated the absorption of bases by a soil from a mixture of various substances in solution—employing for that purpose a solution of a soluble phosphate—and the extent to which the presence of other substances influences the absorption of potash by the soil.

The results of the experiments show that a soil which was capable of absorbing 72 per cent. of the potash from a solution of potassium sulphate was able to absorb only 36·7 per cent. in the presence of other substances in solution, so that there was a diminution of potash absorption equal to 35·3 per cent. The diminishing influence of the other substances in a solution having the following composition in grams per 100 c.c.—

K_2O.	Na_2O.	CaO.	MgO.	P_2O_5.	NH_3.	SO_3.	Cl.
0·0469	0·1373	0·065	0·0326	0·056	0·02	0·1778	0·2137

was found to be as under:—

Total decrease p.c.		NaCl p.c.	SO_4Ca p.c.	Mg salts p.c.	$(PO_4)_2CaH_4$ p.c.	$(NH_4)_2SO_4$ p.c.
35·3	=	13·0	7·0	2·7	3·6	9·0

In explanation of the fact that the presence of a phosphate decreases the absorption of potash, the author considers that the absorption of a phosphate by a soil is the result of a secondary action, and occurs in a manner which is analogous to the absorption of bases from salts, that is to say, a double decomposition takes place between the phosphate and a constituent of the soil, such as potassium or calcium silicate.

Experiment confirmed the supposition that twice as much phosphoric acid is absorbed by a soil from a solution of a superphosphate ($CaH_4.2PO_4$) as from a solution of pure phosphoric acid.

It is well known that a soil which has already absorbed a substance from solution will re-absorb the same substance if again treated with some of the original solution. A point is however reached when the re-absorption ceases; and it is suggested that this point, or the requirements of a soil for certain substances, should in all cases be ascertained. With this object the solution should be percolated through the soil, as thereby more constituents are absorbed than when the usual method of repeatedly agitating the soil with fresh quantities of the solution is followed.

The author's views on absorption agree with those hitherto expressed by other observers, that it is a purely chemical action, and that the degree of absorption for one and the same soil is dependent on the quantity of soil, the quantity of solution, and the amount of substances contained in the solution. Absorptive power is not confined to finely divided soils or to soils alone, for it is possessed by many artificially prepared substances, and even by such compact bodies as marl or basalt. The double silicates containing iron or alumina are the most active constituents in determining the absorptive power of a soil, being even more active than the hydrated silicates or those which are easily decomposed by weak acids.

Soils contain very little phosphoric acid which can be dissolved out by weak acids, owing to the original phosphate after absorption having become by degrees less soluble, in the same manner as iron and calcium phosphates are rendered less soluble by being kept in contact with weak acids. A. J. C.

Experimental Inquiry as to the Quantity of Nitrogen which must be supplied to cultivated Plants to ensure their Normal Development as Field Crops. By Thaer (*Landw. Versuchs.-Stat.*, 23, 377—383).—In this investigation a plot of land of 9 morgens in area (about $5\frac{3}{4}$ acres) was manured during a certain time with artificial manures containing a known amount of nitrogen, and the amount of nitrogen determined in the yearly produce, as shown in the table (p. 569). Hence it appears that during a period of six years $89\frac{1}{2}$ lbs. of nitrogen had been added which gave a total produce yielding 198·69 lbs., or an excess of nitrogen equal to 109·19 lbs., that is only 45 per cent. of the nitrogen in the total produce during that period had been supplied in manure.

In discussing the question, in what manner is the excess of nitrogen (55 per cent.) supplied, the author believes that no excessive accumulation takes place in the soil, but only sufficient is yearly stored there, more or less, according to the requirements of the plant and the amount which has been artificially added.

It is considered that the yearly addition of $12\frac{1}{2}$ lbs. of nitrogen per morgen is the maximum amount required. This amount would give, for a good cereal harvest, 25·3 lbs. as a total nitrogen value in the produce. It will be noticed in the above experiments that in the year 1878, the wheat crop required 33·6 lbs. total nitrogen, or 75 per

	Nitrogen added, lbs.*	Crop.	Corn.	Straw.	Tubers.	Total nitrogen in yearly produce, lbs.
			Centners.†			
1872....	18	Barley	6·5	—	—	10·4
,, ...	—	,,	—	9·8	—	6·27
1873....	52	Potatoes ..	—	—	85	28·90
1874....	—	Oats	9·2	—	—	17·66
,, ...	—	,, ...	—	14·5	—	8·22
		Four-course system was followed.				
1875....	9	Potatoes ..	—	—	75	25·50
1876....	—	Barley	8·5	—	—	13·60
,, ...	—	,, ...	—	13·6	—	8·70
1877....	10·5	Peas	7·4	—	—	26·19
,, ...	—	,,	—	18·6	—	19·34
1878....	—	Wheat	11·2	—	—	23·29
			—	21·5	—	10·32
Total...	89·5		42·8	78·0	160	198·69

cent. of the nitrogen was supplied from other sources than in the manure, and this amount is said to be the maximum amount which can be exhausted by cereals in open field culture. A. J. C.

Analytical Chemistry.

Determination of the Specific Gravity of Powdered Substances. By F. Rüdorff (*Deut. Chem. Ges. Ber.*, **12**, 249—252).—This is effected by a modification of Regnault's method of ascertaining the weight of the substance and the volume of air displaced by it. A diagram of the apparatus employed is given in the paper. It is a glass vessel, consisting of two chambers connected with one another and with a manometer. The upper chamber is closed by a stopper furnished with a stopcock, and contains a small glass vessel to hold the powder; the lower chamber, which terminates in a long tube with a stopcock at its lower end, is partly filled with mercury. The mercury is first allowed to flow out through the long tube until the pressure in the interior of the apparatus is diminished to about half an atmosphere. A precisely similar experiment is then made after a weighed quantity of the powder has been introduced into the glass vessel in the upper chamber. The quantity of mercury which is allowed to flow out is noted in both cases. If m be the difference of

* 1 lb. = 1¼ lb. av. † 1 Centner = 123½ lbs. av.

mercury level in the two limbs of the manometer and b the barometric pressure, $b-m=p$ will be the pressure in the interior of the apparatus. Let q be the volume of mercury let out in the first, and q' that in the second experiment, and v and v' the respective volumes of the contained air, then it is evident $v-v'$ will be the volume V of the powder. If x is the volume of that section of the limb of the manometer in which the mercury has risen,

$$\begin{aligned} V : V + q - x &:: b - m : b. \\ V' : V' + q' - x &:: b - m : b. \end{aligned}$$

from which $v-v' = \frac{(q-q')\ (b-m)}{m}$ or $V = \frac{(q-q')p}{m}$.

The author gives the specific gravities of eleven substances obtained by this means, amongst which are the following: copper sulphate (cryst.), 2·330; oxalic acid (cryst.), 1·531; toluidine, 1·046; thymol, 1·069; asparagine, 1·552. C. E. G.

Estimation of Hydrogen in Gaseous Mixtures. By W. Hempel (*Deut. Chem. Ges. Ber.*, **12**, 636—642).—The method described in this paper is based on the property of occlusion of hydrogen by palladium. The metal is employed in the finely-divided state, and previously to the analysis is covered with a superficial coating of oxide by ignition in the air, the effect of which is to bring about the combustion of a certain quantity of hydrogen, and thus raise the metal to the temperature most favourable to the occlusion of the remainder; 4—5 grams are placed in a **U**-tube, in connection on the one side with the burette containing the gas for analysis, on the other with a gas burette. (These are figured and described, and details are given of the method.) The **U**-tube being surrounded with water at 90—100°, the gaseous mixture, previously freed from constituents removable by absorption by the usual reagents, is passed three times backwards and forwards over the palladium. The difference of volume on a second reading is the volume of hydrogen in the mixture. Specimen analyses are cited of mixtures of marsh-gas, nitrogen, and hydrogen, in demonstration of the trustworthiness of the method. By its means hydrogen may also be accurately separated from mixtures of nitrogen with ethylene and with carbonic anhydride, from aqueous vapour and from traces of ammonia, but not from traces of hydrochloric acid, the vapours of benzene or of alcohol in large quantity, or from carbonic oxide. C. F. C.

Separation and Estimation of Chlorine, Bromine, and Iodine. By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 301—302).—Chlorine, bromine, and iodine, which must be in the form of chlorides, bromides, and iodides, may be separated from each other, and estimated as follows:—

The mixture is slightly acidulated with sulphuric acid, and treated with a slight excess of a mixture of hydrogen, sodium sulphite, and copper sulphate, which precipitates the iodine completely as cuprous iodide, in which form it can be estimated, except in the presence of

thiocyanate. The filtrate from the cuprous iodide is boiled with excess of sulphuric acid to expel sulphurous acid. The solution is placed in a flask with chromic acid or a chromic mixture, and the flask is connected with some Varrentrapp and Will's bulbs (for the estimation of nitrogen or ammonia) containing a solution of hydrogen sodium sulphite, sulphurous acid, or potassium iodide, or carbon bisulphide, and kept cool by water. The contents of the flask are heated, and the bromine expelled is absorbed in the bulbs; it is then estimated as silver bromide or by the colorimetric method. The chlorine is estimated in the residue as silver chloride, after reducing the chromic acid with sulphurous acid. It is necessary to work with care, owing to the number of reactions and operations required in this method.

L. T. O'S.

Preparation of Sulphuretted Hydrogen for Chemico-Legal Investigations. By R. Otto (*Deut. Chem. Ges. Ber.*, **12**, 215—219). —The idea is still entertained by many that arseniuretted and sulphuretted hydrogen cannot be simultaneously formed in the same liquid. So far back as 1869, it was noticed by J. Otto, and has been since confirmed by others, that the gas given off from impure ferrous sulphide and common sulphuric acid may contain arseniuretted hydrogen. The fact may be proved by conducting the gas first through water or alkaline solution, and then through warm pure nitric acid. The residue obtained by evaporating the acid invariably gives traces of arsenic in Marsh's apparatus. Myers (*Annalen*, **159**, 124 and 127) considered that this could occur only when the acid used is impure, but that impurities in the sulphide are of little consequence. According to him, the arsenious oxide (or chloride) contained in the acid is first precipitated as sulphide, and the sulphide subsequently acted on by the nascent hydrogen formed from the metallic iron always present in ferrous sulphide. He proved that freshly-precipitated arsenious sulphide is reduced by nascent hydrogen to arseniuretted and sulphuretted hydrogen; and this statement the author confirms, but states that the fused sulphide is not so attacked. He has found, however, that even when perfectly pure acid is used, arseniuretted hydrogen may still be given off from impure ferrous sulphide.

This is of much importance; for arseniuretted hydrogen will be readily taken up by any liquid containing oxidising agents, such as salts of easily reducible metals. This is particularly to be feared when, as commonly happens, the organic matter of a solution has been previously destroyed by potassium chlorate and hydrochloric acid, and when every trace of chlorine has not been expelled from the liquid. The danger is increased in such cases by the fact that prolonged treatment with hydrogen sulphide is frequently necessary to precipitate even small quantities of metal. This the author attributes to the presence of organic compounds, alterable by the gas, which are formed during the oxidation. He has repeatedly observed that chloral hydrate is produced by the oxidation of flesh or vegetable matter.

To avoid all risk, therefore, he recommends that sulphuretted hydrogen should be prepared by the action of pure hydrochloric acid on pure calcium sulphide, obtained by roasting gypsum with charcoal. A

uniform stream of gas is easily secured by allowing the concentrated acid to drop from a separating-funnel into a flask containing lumps of the sulphide covered with a small quantity of water. The gas being free from hydrogen, a contamination of it with arsenic is not to be feared even when the acid is impure.

Taking these facts into consideration, the question whether arsenic is ever naturally contained in animal bodies is still an open one.

Ch. B.

Action of Ammoniacal Salts on Metallic Sulphides and its Application to Mineral Analysis. By P. de Clermont (*Compt. rend.*, **88**, 972—974).—The sulphides of bismuth, copper, cadmium, and mercury are not attacked by boiling with ammonium chloride. Antimony bisulphide, however, is decomposed, forming ammonium sulphide and antimony trichloride; stannic sulphide yields stannic acid; stannous sulphide, stannous oxide. The sulphides of the metals not precipitated by sulphuretted hydrogen in an acid solution behave in a peculiar manner; those of manganese and iron are completely dissolved when boiled with ammonium chloride, forming protochlorides. The sulphides of nickel, cobalt, and zinc dissolve slowly, zinc sulphide being the most soluble; whilst the oxides of chromium and aluminium are not dissolved. When, therefore, a mixture of the sulphide and oxides of these metals is boiled with ammonium chloride, all the iron and manganese goes into solution together with part of the nickel, cobalt, and zinc, and part remains undissolved with the chromium and aluminium. This would afford a ready method for the separation of iron and manganese from aluminium and chromium in quantitative analysis. Oxalate and tartrate of ammonium both decompose ferrous sulphide, which, with manganese sulphide, is also decomposed by ammonium succinate.

L. T. O'S.

Estimation of Soluble Phosphoric Acid in Superphosphates. By H. Wattenberg (*Landw. Versuchs.-Stat.*, **23**, 374—376).—In the extraction of commercial superphosphates and of pure monocalcium phosphate by the Magdeburg process, in which 144 parts by weight of water are taken to one part of the monocalcium phosphate, the author shows that a greater or lesser quantity of water has practically no effect on the determination of the soluble phosphoric acid. This contradicts Erlenmeyer's statement that the monophosphate is decomposed, except in presence of free phosphoric acid, if the quantity of water taken be less than 700 times the weight of the monocalcium phosphate.

A. J. C.

Estimation of Zinc. By F. Beilstein and L. Jawein (*Deut. Chem. Ges. Ber.*, **12**, 446—448).—Of the methods proposed for the electrolytic estimation of zinc, Luckow's (*Jahresb.*, 1865, 686), Wrightson's (*Zeitschr. Anal. Chem.*, **15**, 303), Parodi and Mascazzini's (*Zeitschr. Anal. Chem.*, **16**, 469), and Riche's (*Ann. Chim. Phys.*), may be used for the estimation of small quantities (10—20 mgrms.). The authors recommend that the zinc should be thrown down from a solution of nitrate or sulphate which has been treated with caustic soda, and the precipitate dissolved in potassium cyanide. The zinc is pre-

cipitated on platinum foil, which is connected with a battery of four Bunsen cells, having zinc cylinders 15 cm. high; in this way about 1 gram of zinc is deposited in an hour. The platinum with the zinc deposit is washed successively with water, alcohol, and ether, dried at 100°, and weighed. The zinc is then dissolved off by hydrochloric or nitric acid, and the platinum dried and weighed. To insure complete precipitation, the electrode is again introduced into the solution, and the operation is repeated until zinc ceases to be deposited. P. P. B.

Mechanical Analysis of Soils. By M. Fesca (*Landw. Versuchs.-Stat.*, **23**, 384).—This is an abstract of the author's paper in which he recommends Schöne's apparatus for the mechanical analysis of soils, by which means they can be classified according to their elutriative value. A. J. C.

New Method for Determining the Melting Points of Organic Substances. By A. Terreil (*Bull. Soc. Chim.* [2], **31**, 155—156).—Instead of taking the melting point of an organic substance in the usual manner, the author prefers to operate as follows. A portion of the substance is melted, and by means of a warm glass thread a single drop of the melted body is placed on the bulb of a thermometer; the latter is then fixed above the flame of a gas-lamp, at such a distance that the mercury rises very slowly. As soon as the substance has melted, the temperature is read off, and the thermometer being allowed to cool, the solidifying point is taken also. From these data the correct melting point is calculated.

The method is said to have the advantage of great rapidity of execution, and not to be liable to errors arising from surfusion; it is necessary, however, with substances which melt considerably above 100°, to use a thermometer with a large bulb, in order that the cooling may take place slowly, otherwise it is difficult to determine the exact moment of solidification. J. W.

Detection of Marsh-Gas in the Air of Mines. By Mallard and Le Chatelier (*Compt. rend.*, **88**, 749—750).—As the ordinary safety lamp is only capable of showing the presence of 3 per cent. of marsh-gas, and 0·892 per cent. forms an explosive mixture with coal-dust, it is proposed to use hydrogen in the safety lamp, by which means the presence of 0·25 per cent. marsh-gas can easily be detected. The blue halo round the flame is more distinct, since it is not concealed by a brighter flame.

The jet of hydrogen is produced from a small hydrogen lamp, substituted for the oil reservoir of a Munseler lamp, the glass cylinder of which is replaced by one of copper, pierced with a lateral opening. Through this orifice the flame can be observed with great accuracy by means of a lens of the requisite focal length. L. T. O'S.

Diagnosis of Fatty Alcohols. By H. Gutknecht (*Deut. Chem. Ges. Ber.*, **12**, 622—625).—V. Meyer having indicated the existence of limits to the applicability of his well known method for the discrimi-

nation of the alcohols (*Annalen*, **180**, 143), the author has endeavoured to fix them. In the secondary series no colour reaction is obtainable with hexyl alcohol: when amyl iodide, however, is treated in the usual way, the chloroform is coloured bluish-green. At this point, therefore, the limit is reached.

In the primary series a fully characteristic reaction was obtained as far as octyl alcohol. Nonyl and the higher alcohols were not investigated. C. F. C.

Bernard's Method for the Estimation of Glucose in Blood. By P. Picard (*Compt. rend.*, **88**, 755—756).—The author points out that whereas there are substances other than sugar in the blood capable of reducing Fehling's solution, yet they are present in such small quantities as not to interfere with the reaction after the separation of the fibrin.

Moreover, this method is preferable to the saccharimetric method, the results of which are in many cases vitiated by the presence of substances other than sugar which possess optical properties.

L. T. O'S.

Estimation of Sugar in Blood. By D'Arsonval (*Compt. rend.*, **88**, 753—755).—This paper is a reply to the objections raised by Cazeneuve against Bernard's method for the estimation of sugar in blood. L. T. O'S.

Test for Tartaric Acid which Distinguishes it from Citric Acid. By Cailletet (*Chem. Centr.* [3], 1879, 14).—A cold saturated solution of potassium dichromate gives with tartaric acid a dark brown colour, and evolves carbonic anhydride. The dichromate solution acts very slowly upon citric acid, and only a light brown colour is produced. If 1 gram of powdered citric acid be added to 10 c.c. of the cold saturated dichromate solution, the orange-red colour of the solution is unchanged after 10 minutes if tartaric acid is absent; 5 per cent. of tartaric acid will produce a dark brown colour, whilst 1 per cent. produces a coffee-brown tint. Vinegar prepared from wine, if heated with an equal volume of the dichromate solution, produces a dark red colour, which is more intense the larger the quantity of tartrate present: if the vinegar is made from fruit, musty beer, wood vinegar, or from anything but wine, this colour does not appear. F. C.

Testing Milk for Starch-Powder. By H. Hager (*Chem. Centr.*, 1878, 783).—If starch is present in milk, iodine does not yield with it the blue coloration at once, because the lactoproteïn bodies combine with the iodine, and decolorise the solution. Iodine solution must therefore be added until the milk is yellow; the milk is then thoroughly shaken, and more iodine solution is added if the yellow colour has disappeared: this process is repeated, until after agitation the milk appears either yellow, showing the absence of starch, or blue. If the starch has been stirred into *cold* milk, it can be obtained by subsidence and detected. F. C.

Marchand's Method of Determining the Butter in Milk. By C. Méhu (*J. Pharm. Chem.* [4], **29**, 16—18).—The author's experience in the use of Marchand's lacto-butyrometer leads him to question the accuracy of the results obtained by it. He criticises the account given of the process by Marchand, in which the state of purity of the ether employed is not given, and apparently one set of tables only is furnished, whilst alcohol of two different strengths is employed: further, *a drop* of caustic soda-solution is an indefinite quantity to add. A frequent cause of error arises from milk being boiled after addition of sodium carbonate in order to prevent change in hot weather; milk so treated often gives no evidence of free butter by the lacto-butyrometer, Marchand's method often yielding a quantity of butter less than 12·6 grams per litre, when the gravimetric method yields 30 grams of fatty matter. The author has obtained by Marchand's method results pretty concordant with the results obtained by weighing, when he substitutes 90 p. c. alcohol saturated with boric acid for ordinary alcohol, and he frequently has added boric acid to the milk in the proportion of 2 grams to the litre: this boric acid is added instead of sodium carbonate.

It must be remembered that in any case the fat separates very slowly from boiled milk. The author considers that Marchand's method is valuable only for making a preliminary trial of the milk, and if the milk is not proved of good quality the test should be repeated after the addition of 2 or 3 grams of boric acid per litre to the milk; in any case a gravimetric analysis should follow in all analyses where adulteration has to be proved. F. C.

Adulteration of Beeswax. By Buchner (*Dingl. polyt. J.*, **231**, 272).—On account of the high price of beeswax, it is often largely contaminated with talc or resin. For several years cerosin has been added to beeswax in large quantities, as much as 33 to 50 p. c. having been found. This substance is a mixture of purified ozokerite and carnauba wax, and resembles beeswax in appearance. Its presence may be detected by the sp. gr.; that of the adulterated product being lower than that of pure beeswax. The sp. gr. of yellow raw beeswax is 0·959, of white wax 0·955. Since carnauba wax imparts to cerosin its hardness, soft cerosin is lighter than the hard wax, the density of carnauba wax being 0·999. To detect admixture of cerosin, the wax is boiled in a test tube with a concentrated alcoholic solution of potash (1 pt. KHO in $2\frac{1}{2}$ to 3 pts. 90 p. c. alcohol) for a few minutes, and kept in the water-bath for some time to prevent the mixture from solidifying. The solution will remain clear if the wax is pure, but paraffin floats on the surface if it is adulterated with cerosin.

D. B.

Technical Chemistry.

Preparation of Carbonic Anhydride under any Desired Pressure. By H. Beins (*Chem. Centr.* [3], 1878, 832).—Sodium bicarbonate evolves carbonic anhydride when heated even under great pressure. On this principle the author prepares liquefied carbonic anhydride, or "carboleum," which he applies for various purposes, amongst others as a motive power.

The bicarbonate is placed in a retort consisting of two concentric iron tubes, a red hot iron being pushed up into central tube, and causing the evolution of the gas. The gas freed from water by a condensing arrangement, passes into a reservoir provided with a pressure gauge, and is liquefied by its own pressure. F. C.

Antichlor. By G. Lunge (*Deut. Chem. Ges. Ber.*, **12**, 404—407).—Fordos and Gélis (*Rep. Chim. Appl.*, 1859, **1**, 384) who first proposed the use of hyposulphite (thiosulphate) as an antichlor, regarded its action as expressed by the following equation:—$Na_2S_2O_3 + 8Cl + 5H_2O = Na_2SO_4 + 8HCl + H_2SO_4$ (1). The following equations have also been proposed as expressing the reaction:—$Na_2S_2O_3 + 2Cl + H_2O = Na_2SO_4 + 2HCl + S$ (2). $2Na_2S_2O_3 + Cl_2 = Na_2S_4O_6 + 2NaCl$ (3). The value of hyposulphite is, however, usually calculated according to equation (1), *i.e.*, 1 kilo. hyposulphite as neutralising 1,144 grams chlorine.

Experiments made with hypochlorite and hyposulphite, in which the latter was present in excess, show the reaction to be more complicated than is indicated by any of the above equations. The chief action, however, is expressed by equation (3), although some is decomposed according to (1). When the alkaline solution is diluted, it becomes acid, and sulphuretted hydrogen is evolved. The formation of sulphuretted hydrogen is explained by supposing that some hyposulphite is decomposed into sulphide and trithionate, thus:—$2Na_2S_2O_3 = Na_2S_3O_6 + Na_2S$ (4). The former is decomposed by the acid set free in reaction (1) with the formation of hydrogen sulphide; at the same time sulphur is deposited by the decomposition of the trithionate. These reactions have the combined effect of lessening the power of the hyposulphite to such an extent that as a final result 1 kilo. neutralises only 145 grams of chlorine. In cases where an excess of hypochlorite is used, the final result is that 1 molecule of hyposulphite scarcely neutralises 1 atom of chlorine.

The author has also investigated the value of ammonia as an antichlor. Koll, who proposed it, regarded its action as expressed by the equation $4NH_3 + 3Cl = N + 3NH_4Cl$. Experiments show, however, that twice or three times as much ammonia is required, and even in cases where ammonia is present in excess, long continued standing fails to complete the reaction, which only occurs on boiling. Further, its use as an antichlor is rendered impracticable, owing to the formation of compounds having an odour like that of chloropicrin.

P. P. B.

Application of Gas Liquor to the Production of Potassium Carbonate and other Salts. By R. W. Wallace and C. F. Claus (*Chem. Centr.*, **3**, 1878, 832).—In the preparation of ammonium salts from gas liquor, the liquor is submitted to a distillation by steam; this carries over not only ammonia, but also ammonium carbonate and sulphide, into the acid absorbing solution, and consequently carbonic anhydride and hydrogen sulphide are liberated. The authors conduct these gases through towers containing potassium or sodium sulphide solution, which is thus converted into carbonate, and hydrogen sulphide alone escapes. Another process consists in passing the ammoniacal vapours through potassium sulphide solution before they reach the acid; potassium carbonate remains in solution, and ammonium sulphide passes on to the acid, from which the only gas evolved will then be hydrogen sulphide. A third process consists in mixing the gas liquor with potassium carbonate before it is distilled, potassium carbonate containing a little potassium thiocyanate is then left in the residual liquor. The hydrogen sulphide escaping in any of these processes is burnt to sulphurous anhydride, which is used for making sulphuric acid, or is conducted into ammonium sulphide for the preparation of ammonium thiosulphate. The authors also claim the use of the hydrogen sulphide for precipitating copper, silver, and lead from their solutions. The construction of furnaces of bauxite is further claimed to be used for the reduction of alkaline sulphates by charcoal to yield the alkaline sulphide required in some of the above processes.

F. C.

Soda Industry. By G. Lunge (*Dingl. polyt. J.*, **231**, 266—272).—In comparing Leblanc's with the ammonia-soda process, the author mentions that in England only one firm uses the latter, as proposed by Solvay, whilst Leblanc's process still appears to be worked more profitably, as the hydrochloric acid obtained as a bye-product is of the greatest advantage to soda manufacturers. Solvay has not yet succeeded in preparing hydrochloric acid from the calcium and magnesium chlorides formed in his process. In France, the ammonia process has made rapid progress, probably owing to the fact that Solvay himself is a large soda manufacturer.

Solvay recently stated that his process would soon replace the Leblanc process completely, and that the latter would merely be of historical value. The author contradicts this statement. There is but little doubt that at places where salt can be obtained as a strong brine, the ammonia soda process is the best at the present time, but so long as hydrochloric acid plays an important part in the revenue of soda works (and this is the case with most German manufacturers), Leblanc's process will certainly be retained. Moreover, on account of the high price, and the limited production of ammonia, Solvay's process could never be extended very largely. Solvay claims the advantage that in his process no emanations of gases and liquids are produced which are injurious to health, whereas in Leblanc's process, through insufficient condensation of the hydrochloric acid and the residual liquors, nuisances frequently occur, which are regarded as a calamity in the centre of the English soda manufacture. With regard to the escape of hydrochloric acid, the author mentions that since the

institution of inspectors in England the condensation apparatus have been perfected to a great extent, and that the same evil would exist, if it were possible to manufacture hydrochloric acid by Solvay's process. The nuisances arising from the acid manganese liquors in Leblanc's process are now entirely prevented by the general introduction of Weldon's recovery process, and it is only the residual liquors in the soda lixiviation which occasionally give rise to disagreeable effects in England. This could, however, be avoided if, as is the case in most continental works, the recovery of the sulphur was undertaken.

Weldon has recently patented various mechanical improvements in the old sodium sulphide carbonic acid process, and although a large sum of money has been expended in the trials, the results were unsatisfactory. To resist the powerful action of sodium sulphide on all materials hitherto employed, Weldon lined his furnace with bricks made of coke-dust and tar under high pressure, and subsequently burnt. The oxidation of the sodium sulphide formed was prevented by a peculiar construction of the furnace, whereby it was possible to work with almost pure carbonic oxide, a perfectly pure sodium sulphide being obtained. The treatment of the latter with carbonic acid was arranged so systematically as to use up the whole of it, whilst a gas was obtained rich in hydrogen sulphide. The latter was absorbed by iron oxide, and the sulphide formed re-worked into sulphur and iron oxide by a blast of air. However, it was found that the pure sodium sulphide produced was infusible, and could not be removed from the furnace. By introducing air and rendering the sulphide more fusible, the heat produced was so great, that it destroyed the carbon bricks of the furnace in a very short time. D. B.

Preparation and Use of a Highly Siliceous Pig-iron. (*Dingl. polyt. J.*, 231—283).—Hitherto it has not been considered possible to eliminate phosphorus from iron in the furnace, a circumstance which Pechin contradicts (*Metall. Review*, 1878, **1**, 515). The pig-iron used contains a large quantity of silicon, the flux being limestone of the following composition :—

SiO_2.	Fe_2O_3.	$CaCO_3$.	$MgCO_3$.
4·1	1·2	91·2	3·21

The iron after treatment contains :—

Si.	P.	S.	Graphite.	Combined carbon.
8·239	0·007	0·013	2·045	0·635

while the slag consists of—

SiO_2.	Al_2O_3.	MgO.	CaO.	Mn.	P_2O_5.	S.	Fe.
43·08	11·62	2·35	37·13	2·90	0·23	1·92	0·32

As only a small proportion of the phosphorus is found in the iron or cinder, it is evident the greater part must escape through the top of the furnace. Riley has shown that pig-iron containing 20 p.c. silicon is free from carbon, and that an increase in silicon diminishes the

quantity of carbon in iron. It is therefore not improbable that this fact applies also to the phosphorus in iron. Akerman has shown that the quantity of phosphorus decreases the higher the temperature is raised in the furnace. D. B.

Malleable Iron at the Paris Exhibition of 1878. (*Dingl. polyt. J.*, **231**, 274—278).—The last exhibition at Paris clearly showed the vast improvements which have been made in the methods of preparing malleable iron. Weld-iron, a product obtained in a pasty condition, and therefore contaminated with slag, is now replaced by "run-iron," a product obtained in a fluid state, and therefore free from slag, and perfectly uniform in quality, but the run-iron is made by the Bessemer and the Siemens-Martin processes. The following three difficulties are met with:—(1.) The quantity of phosphorus in the ores. (2.) The difficulty of producing compact castings. (3) The difficulty of welding run-iron.

I. The first difficulty may be overcome in various ways.

(1.) By the importation of foreign ores. The ores of the south of Europe and north of Africa are very rich in iron, and almost free from phosphorus. Large quantities of ore are imported into France, England, and Germany.

(2.) By dephosphorising the iron.

a. By refining pig-iron according to Bell's method, which is known to all. Although this method has solved the problem of dephosphorisation, another step towards improvement is yet wanted, viz., dephosphorising iron without having to remove the silicon.

b. In puddling. The removal of phosphorus by this process can be regarded only as forming part of the run-iron process, inasmuch as the dephosphorised iron is used as a flux in the reverberatory furnace.

c. By the direct extraction of iron from the ores, according to Martin's process. Du Puy's new method is preferable, however.

(3.) By dephosphorisation according to the ferro-manganese process, which is based on the circumstance that the injurious action of phosphorus is decreased with the quantity of carbon in iron.

II. The difficulty of producing compact castings is now entirely removed, the method of deoxidation with manganese, silicon, and other substances having been perfected to a great measure. Although silicon forms the best agent, an excess injures the quality of the steel.

III. Welding run-iron. This difficulty has now been surmounted. The welding property of iron increases and diminishes in the reverse ratio to the carbon contained in iron, but it reaches its limit more quickly than the malleability does, a circumstance which explains the reason that highly carbonaceous iron can no longer be welded.

In conclusion it may be stated that the use of malleable iron has been vastly extended through the general application of run-iron, and that owing to the great purity which can be guaranteed, this article will become of great importance in the future iron industry, especially as all the difficulties experienced in the commencement have now been entirely overcome. There is but little doubt that numerous applications will be found for this article. D. B.

A Thread-like Substance found in the Excavations of Pompeii. By S. de Luca (*Compt. rend.*, **88**, 694—697).—This substance, which has a black colour and is almost completely carbonised, has a coaly lustre and consists of twisted threads, which are severally made up of about twenty fibrous bundles, each comprising five vegetable fibres. These fibres are slender cylinders, supporting each other after the manner of cortical fibres of textile plants. It is easily reduced to a powder by pressure between the fingers, and burns slowly, leaving a white ash; this has an alkaline reaction, and evolves carbonic acid when treated with acids. The ash (18·5 per cent. of the total weight) contains about 21 per cent. of soluble matter, chiefly potassium carbonate; and the remaining 79 per cent. consists principally of silica and lime. The original substance when heated to 110° C., loses 14·5 per cent., and on ignition 67 per cent. By heating in a tube free from air, the gas evolved consisted of carbonic anhydride, carbonic oxide, and traces of hydrogen and nitrogen, an alkaline liquid distilling at the same time.

Its composition, as shown by various analyses given by the author, differs essentially from that of flax or hemp; it has, however, been subjected for eighteen centuries to the action of different natural agents, which in absence of light produce great and varied changes.

It is probable that this flax or hemp of Pompeii was used for surgical purposes, as some rude surgical instruments were found in its vicinity. L. T. O'S.

A Process for Utilising the Residue from the Manufacture of Potassium Ferrocyanide. By Gawalovski (*Chem. Centr.* [3], 1879, 14—16).—The author's process applies to the sediment left after the soluble salts have been almost completely extracted by water from the furnace product. The sediment consists chiefly of charcoal, iron oxide and some iron; it sometimes gives as much as 15 per cent. of soluble salts containing from 1 to 5 per cent. of potassium ferrocyanide. The product has been sold as a manure, but the author maintains that it will be found more profitable to extract the soluble salts and iron, and to sell the purified charcoal residue for decolorising sugar, oil, &c. The soluble portion of the sediment contains besides the potassium ferrocyanide, alkaline suphates, sulphides, sulphocyanide, and traces of chlorides; but these salts when left exposed in layers to the air effloresce and are decomposed by weathering, the iron and iron oxide colouring the mass grey or brown. The percentage of ferrocyanide is too small to pay for extraction, but the author finds that it can be utilised by first treating the sediment with water, then filtering and dissolving the iron away from the charcoal by treatment with hydrochloric acid: the charcoal is then thoroughly washed and furnishes a pure black powder for sugar refining. The water and the acid solutions are mixed, and the Prussian blue thus precipitated is filtered off. This filtrate deposits a crystalline sediment of alkaline sulphates, and leaves a liquid containing ferric sulphocyanide and chloride: by adding to this liquid potash solution and potassium sulphide solution, it may be further made to yield potassium sulphocyanide. The original sediment should be thoroughly soaked and mixed in wooden tubs, with

from one half to an equal weight of water, and filtered through wooden presses: the insoluble residue, after treatment with hydrochloric acid, should be separated by leaden presses. The residual charcoal when dried, powdered, and sifted, is ready for use. F. C.

On Making Red Wine. By F. Kernlter (*Chem. Centr.*, 1874, 784).—The must may during fermentation become so much heated that the process is very much hindered, or even arrested: this phenomenon is due to a paralysis of the yeast caused by the effervescence. The danger is connected with all conditions of a more intense fermentation, especially depending on the quantity of liquid fermenting in one vessel, on the consistency of the must, and on the original temperature of the must and of the place in which it is fermenting. The precise limit of temperature at which the yeast is injured depends on the length of time during which the fermentation has proceeded, on the quantity of alcohol already formed, and on other conditions: it cannot therefore be definitely laid down; it cannot be lower than 35°, and is generally above 40°. The fermentation, on becoming sluggish, is best quickened by addition of fresh yeast. The soluble constituents of the stalks tend to impede the fermentation and to hinder overheating: the overheating is, however, more certainly prevented by fermenting in small vessels, by constant beating down and stirring in the film which forms on the surface, and by ventilation of the fermenting-room. The stalks impart an unpleasant taste to the wine, and should always be removed. F. C.

Pressing of Red Wine. By Nessler (*Chem. Centr.* [3], 1879, 14). —The solution of the red colouring matter depends on the temperature. At 0—10° the liquid becomes only slightly coloured; at 15—20° a strong colour is imparted: at the latter temperature from 8 to 10 days are sufficient to completely dissolve the colouring matter. The skins must always be kept beneath the surface, and, especially at the higher temperatures, exposure to the air must be avoided to prevent formation of acetic acid. Sinking bottoms must be used to prevent the upper stalks becoming mouldy, if low temperatures and late pressing are adopted. In the south of France the fermenting liquid is left for 4 or 5 days, in contact with the stalks and skins, at a temperature of 20—30°. Kageneck warms his fermenting cellar to 16°, and thus succeeds in obtaining a good dark wine, by pressing after 8 days. The author considers 15—18° a suitable temperature, but good results have been obtained when a temperature of 35° was employed. F. C.

Plastering of Wine. By E. Pollacci (*Gazetta chimica italiana*, **8**, 379—388).—In the south of France it has been the custom from ancient times to add plaster to wine or to the must, with the object of brightening the colour, and to render the wine capable of sustaining long voyages without undergoing change. From France, the practice passed into Spain and Portugal, and subsequently into Sicily and into Sardinia. It was not, however, until the year 1853 that the use of plaster became general in this locality. According to the author, the plaster is added to the grapes in the tun, being sprinkled over the layers of

grapes in the proportion of about 1—3 per cent.; as, however, it is not usually weighed and costs but little, it is frequently added in larger quantity than that just indicated. The present paper contains an account of an elaborate series of experiments made to ascertain the effect of adding plaster and pure calcium sulphate to wine, reserving its effect on must for a subsequent communication. A white wine from S. Colombano at Lambro was employed, dry and limpid, and the results obtained show that the calcium sulphate reacts solely on the cream of tartar, producing potassium-hydrogen sulphate, which remains in solution, and calcium tartrate, which is precipitated for the most part. This reaction, however, is only partial, as the wine still contains not only calcium sulphate, but also cream of tartar equal to about half that originally present. With pure calcium sulphate, the degree of acidity of the wine remains about the same as it was before treatment, but with common plaster which contains calcium carbonate, it is reduced. Plastered wine, generally speaking, may be regarded as a saturated solution of calcium sulphate and tartrate, still retaining the natural constituents of the wine, and also containing potassium hydrogen sulphate (about 1 gram per litre): it must be remembered, however, that the calcium salts mentioned are more soluble in plastered wine than in pure water. On evaporating to one tenth of its bulk plastered wine, or dilute alcohol in which pure calcium sulphate and potassium hydrogen tartrate have been allowed to react, a residue is obtained containing free sulphuric and tartaric acids. It has yet to be ascertained whether these acids are formed by the reaction between the two salts, or by secondary reactions during concentration of the solution. Thus, a small proportion of free sulphuric acid, found in an evaporated wine, cannot be considered as evidence of adulteration. The addition of plaster to wine already fermented, although the most simple and least hurtful form of plastering, profoundly alters the composition of the wine, introducing into it about a gram of potassium sulphate per litre, besides a not inconsiderable quantity of calcium sulphate and tartrate. C. E. G.

Cerium Aniline Black. By H. Bührig (*Dingl. polyt. J.*, **231**, 77—81).—K. Kruis first called attention to cerium aniline black (*ibid.*, 1874, 212—347) as the most beautiful and fastest aniline black known, but, owing to the high prices of cerium salts, it has not hitherto been employed generally in calico printing, and inasmuch as minute quantities of vanadium salts produce more efficient results than the same proportion of cerium salts, the former have obtained the preference; the cerium salts can, however, now be produced at less cost than the vanadium salts, and they produce incomparably better results, so that altogether the cerium black may now be produced at less cost than the vanadium black.

The cerium salts can easily be prepared by the calico printer himself, direct from the mineral cerite. This mineral occurs in great abundance in a bed of copper pyrites in gneiss, at Riddarhytta in Westmannland, Sweden, in hard, fine-grained, very firmly adherent, aggregate masses, of pearl-grey colour. Its sp. gr. is 4·9 to 5·0, and its hardness 5·5.

The following gives the percentage composition of cerite, according to three different authorities, viz.: Hermann, I; Kjerluf, II; Rammelsburg, III.

	I.	II.	III.
Silica	21·346	31·300	19·180
Cerium monoxide	60·987	58·500	64·550
Lanthanum oxide	3·514	8·470	7·280
Didymium oxide	3·105		
Ferric oxide	1·457	4·980	1·540
Lime	1·649	1·230	1·310
Water	6·310	5·520	5·710
Carbonic acid	0·832	—	—
	100·000	100·000	99·570

Besides the above, copper, lead, magnesia, and alkalis have been shown to exist in cerite.

The cerium salt necessary for the preparation of the aniline black is most easily obtained by acting on the cerite with sulphuric acid. 1 kilo. of the mineral in fine powder is treated in a leaden vessel with 1 kilo. of English sulphuric acid, and allowed to stand for several hours in a warm place, the mixture being stirred from time to time. The mass swells up considerably, developing so much heat that part of the sulphuric acid is evaporated, and a clear grey, dry compact product is obtained. This is powdered, and again mixed with 250 to 300 grams of sulphuric acid, and left in a warm place for several days. The leaden vessel is then placed on a sand-bath, and heated for some hours over an open fire, until the excess of sulphuric acid is completely evaporated, and a clear grey powder remains. This treatment is sufficient to ensure the complete decomposition of the cerite.

The soluble sulphates are then extracted by dropping the powder into cold water in small quantities at a time, with constant stirring, and keeping down the temperature by the occasional addition of small pieces of ice (if the temperature rises too high, the powder is apt to form into hard cakes, which cannot be thoroughly lixiviated).

The water is allowed to remain in contact with the salts for a day or two, with occasional stirring; it is then decanted and filtered, and fresh water added to the residue, and the same process repeated, until all the soluble salts are removed. The washings are all mixed together, and this liquor may be employed directly in the preparation of the aniline black; or it may be evaporated and left to crystallise, when clear, rose-coloured crystals separate out.

From 1 kilo. of cerite, 20 litres of liquor were obtained as an average, containing 663·7 grams of cerium oxide, contaminated with small quantities of lanthanum and didymium salts.

In the calico-printing works of Jacob Lytsche, in St. Petersburg, cerium aniline black has been made for more than a year, with the best results. The above process is the one followed by him for the preparation of the cerium salt, and the following is the mixture employed for printing:—

White starch	14 kilos.
Lightly "calcined" starch (British gum)	6·5 „
Water	110 litres.
Sal-ammoniac	1,900 grams.
Potassium chlorate	3,100 „
Aniline salt	6,150 „
Cerium sulphate liquor	10 c.c.

After printing, the cloth is hung up in an "ageing room," kept at a temperature of 38° to 43° C. for eight hours; it is then passed through a weak soda-solution, and lastly thoroughly soaped during half an hour. The same depth of colour may be obtained by using less cerium salt, but in that case longer time is required in ageing, and the colour is not so beautiful.

The same depth of colouring may be obtained under the above-mentioned conditions by adding 50 c.c. of a solution of vanadium chloride (containing 28·35 grams of the salt to the litre of water), equivalent to 0·7985 gram vanadic acid to 100 kilograms of the colouring material, but it does not possess the charming deep blue-black tint of the cerium black.

It has not yet been clearly demonstrated that the other metallic oxides present along with the cerium, especially lanthanum and didymium oxides, do not exercise a disturbing effect on the development of the colour.

Lastly, it may be remarked that cerium aniline grey shows a more beautiful tone than vanadium aniline grey. W. T.

Value of Certain Chemical Agents in Dyeing with Aniline Black. By G. Witz (*Compt. rend.*, **88**, 816—817).—This is a criticism on the results published by Grawitz, the author condemning the use of chromates, and upholding that of vanadium in the formation of aniline black. The author's results for the most part contradict those of Gravitz. L. T. O'S.

A Black Lac for Metal and Wood.—A mixture is made of 500 grams of methyl alcohol and 90—100 of gum lac in powder; in a separate vessel 500 grams of coal tar benzene are mixed with 100 of asphalte. Both mixtures are stirred occasionally for 2 or 3 days, then mixed together in equal parts and lamp black added. The mixture can be made thinner if necessary, by adding a mixture, in equal proportions, of alcohol and benzene. F. C.

General and Physical Chemistry.

Spectra of the Elements and their Compounds. By G. Ciamician (*Wien Akad. Ber.*, **76**, 499—517). **Influence of Temperature and Pressure on the Spectra of Vapours and Gases.** By G. Ciamician (*ibid.*, **77**, 839—841).—In the first of these papers the author says that while he was engaged in some investigations on the spectra of compound bodies, a paper by J. Moser appeared (*Pogg. Ann.*, **160**, 179), in which it is stated that absorption spectra are alone of value in this particular line of research. The author's experience led him to come to a contrary conclusion, and made him extend his investigations, in the course of which the existence of some peculiar relations between the spectra of analogous elements became apparent.

As regards the spectra of compounds, the author comes to the following conclusion; that these spectra are always band spectra, which he thinks may be accounted for on Helmholtz' theory, that molecules give band spectra and free atoms line spectra. Moreover, he considers that it is not every compound which possesses a characteristic spectrum; the compounds of the alkali-metals and lithium have for instance no characteristic spectra, whilst barium oxide has an extremely feeble one. Magnesium, zinc, cadmium, mercury, and silver have no spectra in their compounds. Many of the elements have only compound spectra for their oxides, and show it whatever may be the salt employed in solution.

The author ascribes the absence of compound spectra of so many of the elements to one of two causes. Either that the wave-length of one of the two elements forming the compound is so much more intense than the other, that the decomposition of the molecule ensues almost immediately, and the line spectra are at once produced; or, the compounds are not volatile, in which case a continuous spectrum alone is produced.

With regard to the spectra of elementary bodies, Ciamician after observing the spectra of 31 elements, comes to the conclusion that the lines in the spectrum of chemically analogous elements correspond, either singly or in groups; therefore every group of elements has a spectrum which only differs from that of the various members of the group in that the homologous lines or groups of lines are transposed either in one direction or another; *i.e.*, that the wave-lengths increase or decrease, and that sometimes certain lines or groups of lines pass into the ultra-red or the ultra-violet.

Every element possesses also certain lines peculiar to itself, which are generally weaker than those characteristic of the group. The increase or decrease of the wave-lengths of homologous lines in chemically analogous elements he considers to depend on the intensity of the chemical energy of those elements.

It has long been the aim of chemists to express the properties of the

elements as functions of their atomic weights. From these investigations it would appear that they are also functions of the wave-lengths of their spectrum lines.

In the second of these papers, the author investigates the behaviour of the spectra of the greater number of the volatile metalloïds and also of mercury and sodium, under pressure. The three halogens, when the pressure is increased, give rather less distinct lines and a continuous spectrum increasing in brilliancy with the pressure. Sulphur does not seem to change in any way, except that a continuous spectrum appears especially in the red. Phosphorus and arsenic do not seem to change in the least. In mercury, the green and violet are very much widened, and in the case of sodium, the reversed double D line appears on a continuous spectrum. J. M. T.

The Passage of the Galvanic Current through Iron. By Auerbach (*Ann. Phys. Chem.* [2], **5**, 289—344).—When a circuit consisting partly of a straight iron wire, and containing a battery, is closed, the current is at first smaller than the normal current, through what is termed an "extra current," in opposition to the main current. On opening the circuit on the other hand, the current is greater than the normal, the "extra current" being in the same direction with the main current.

Wiedemann and others have explained this extra current as arising from circular magnetisation in the conductor. The lines of magnetic force due to the current are circles surrounding the axis of the conductor, and the current, will therefore tend to magnetise the iron wire conducting it circularly: when it is first established, work has to be done to turn the molecules into their new position, the energy being supplied by the current which is therefore weakened. On the circuit being opened, the molecules return to their old position, and give back this energy, thus strengthening the current. Longitudinal magnetisation of a conductor also affects the current by altering the resistance to it, although observers have differed not only as to the quantity, but even as the quality of this effect. In this paper the author gives the details of a great number of experiments he has made on these two sets of phenomena, as well as some theoretical considerations concerning them, considering them as closely connected, and treating both as due to an alteration in resistance.

He lays down as a general principle (of which Clausius' Second Thermodynamic Law is only a particular case) that no force is in the state "by itself" to bring about conditions which are more favourable to its own operation than those which it found. If then a current pass through an iron wire which it magnetises circularly, it cannot lessen the resistance. If it alter it at all, it must increase the resistance.

As an experimental confirmation of this, he found that the resistance of an iron wire increased with the increase of the current passing through it, and far more than could be accounted for by rise of temperature, that is, the stronger the current, the greater the circular magnetisation, and therefore the greater the resistance. In connection with this, it is pointed out that the true resistance of iron comparable

with that of other metals can only be found by an indefinitely weak current, whose magnetising effect may be neglected.

With longitudinal magnetisation, the resistance was sometimes less, sometimes greater, than with unmagnetised iron. For instance, with hard steel longitudinally magnetised, the resistance was less. The resistance therefore continually increases as the state changes from a saturated longitudinal magnetisation through an unmagnetised condition to a saturated circular magnetisation. In iron and soft steel, longitudinal magnetisation, like circular magnetisation, increases the resistance, which is therefore least for the unmagnetised state.

Other phenomena connected with the resistance of iron were also observed, and are discussed at length in the paper. J. H. P.

Sketch of the Atomic Theory of Heat. By C. Puschl (*Chem. Centr.*, 1879, 90—96; 104—111 and 119—124).—In this paper the author says that at present the received theory is that the heat of a gas consists in the energy of its ponderable atoms, which by their motion and contact in the intervals which separate them, produce the pressure of the gas. In this deduction, the existence of the ether is not taken into consideration, therefore it is assumed that this medium exercises no influence on the atoms. In the same way, the heat of solid or liquid bodies is assumed to consist of the energy with which their atoms attract or repel each other, and the ether in this case also is assumed to have no influence.

Puschl holds that although this theory may be simple, it does not take into consideration all the phenomena which may be observed. For instance, it is a fact that a warm body can lose heat, not only by contact but also by radiation, and the rate of cooling by this latter is often extremely rapid; evidently the atoms of the heated body lose energy to the ether, which therefore must have a resistance of considerable intensity; inversely, a body can also receive heat through radiation as well as by contact; in this case, the atoms receive energy from the ether; therefore in a body cooling by radiation, the motion of its atoms is retarded by the ether, and in a body heated by radiation, the motion of its atoms is accelerated by it. When a body is kept at a constant temperature by means of reciprocal radiation, the accelerating and retarding effects are balanced.

The kinetic theory he considers to be incapable of explaining a rapid destruction or production of atomic motion, by means of the simple production or destruction of ether waves, whilst the author's actinic theory gives such an explanation. The heat of every body consists in great part in radiant heat diffused among its atoms, that is, in the energy of the inter-atomic ether. This medium, on being made to vibrate by means of the accumulated rays, exercises an intense energy on the atoms by means of the difference in radiation; that is by the inequality of elasticity in the opaque atoms, which changes according to their positions, so that they are accelerated or retarded according to their momentary position; and therefore the energy of the atoms is employed to produce ether waves, which in their turn are absorbed to produce energy.

If the movement of the atoms of a body is caused by its radiant

heat, this may explain the transmutation of thermal conductivity through its mass; upon which the diffusion of radiant heat, on account of its great concentration and the slowness of its progression, appears to have no influence.

Besides the movements atoms may have as units, the author considers that the substance of which they are composed, which can only be considered as approximately rigid, may during these disturbances be in a certain state of movement by means of which infinitesimal inter-atomic ether waves are produced, the spectra produced by these varying with the structure of the atoms. J. M. T.

Specific Heat of Uranoso-uranic Oxide and the Atomic Weight of Uranium. By J. Donath (*Deut. Chem. Ges. Ber.*, **12**, 742—745).—The author has determined by means of the Bunsen ice calorimeter, the specific heat of uranoso-uranic oxide prepared from pure uranic acetate, and gives 0·07979 as a mean of four determinations. Taking the specific heat of oxygen as 0·25, then the specific heat of uranium is 0·0497, which when multiplied by 120, yields 5·96 as the atomic heat. This determination corresponds with the atomic weight 120 for uranium; it also shows the molecular heat of uranoso-uranic oxide to be 33·9, thus associating it with similar oxides, *i.e.*, magnetic oxide of iron.

In conclusion, the author comments upon some of the disadvantages of Bunsen's calorimeter. P. P. B.

Heat-Capacity of Mixtures of Methyl Alcohol and Water. By E. Lecher (*Wien Akad. Ber.*, **76** [2], 937—946).—The author employed the same process for determining the heat-capacity as that proposed by Pfaundler (*ibid.*, **59**, 1869), coming to the conclusion, that the heat-capacity of water between 0° and 15° C. being taken as = 1, those of the mixtures of methyl alcohol and water were found to be as follows:—

Alcohol per cent.	Heat capacity.
0 (pure water)	1·000
12·32	1·073
20·42	1·073
30·51	0·980
36·62	0·918
42·64	0·879
51·64	0·826
63·43	0·781
91·14	0·647
100·00 (pure alcohol)	0·622

The author remarks that although these numbers do not follow any simple law, yet they show a series analogous to that given by ethyl alcohol. He also adds that, after he had finished his experiments, Dupré's paper (*Proc. Roy. Soc.*, 1872) came into his hands, in which very different results are obtained. The author has repeated the experiments with great care, obtaining as nearly as possible the same results as above

stated, and he therefore thinks that the methyl alcohol employed by Duprè must have differed from that used by himself and others. J. M. T.

Freezing Mixture of Calcium Chloride and Snow. By H. Hammerl (*Wien Akad. Ber.* [2 Abth.], **78**, 59—79).—The original paper gives tables of the following:—

I. The solubility of the salt at different temperatures.

II. The lowering of the freezing point of the solutions with different proportions.

III. The specific heat of the salt and of the solutions.

IV. The heat of solution with different quantities.

V. The minimum of temperature attainable.

VI. The amount of heat absorbed with different proportions in the mixture.

The lowest temperature theoretically obtainable by admixture of crystallised calcium chloride and ice is − 54·9°, and corresponds with the formula $CaCl_2 + 6H_2O + 8{\cdot}45H_2O$: in order to attain this, dry *snow* in the requisite proportion must be used, and the crystallised calcium chloride must be finely powdered and cooled below 0°. W. S.

Preliminary Study of the Action of Acids on Salts without the Intervention of a Solvent. By M. Lorin (*Compt. rend.*, **88**, 1029—1032).—The author has studied the action of various acids on salts with reference to the thermal changes involved. He has employed sulphuric, formic, valeric, oxalic, tartaric, and other acids, and the salts of these acids with various bases. In all cases the results indicate a chemical action more or less marked, which, for the fatty acids, decreases as the amount of carbon increases. In some cases the disengagement of heat and the maximum effect are instantaneous; in others the reaction seems to take place in stages. Sometimes a considerable time elapses before any rise of temperature is noticed. The products are in many cases solid. C. H. B.

Heat of Hydration of Sodium Oxide, and the Action of Sodium on Sodium Hydroxide, and of Hydrogen on Sodium Oxide. By Beketoff (*Deut. Chem. Ges. Ber.*, **12**, 856).—Sodium does not act on sodium hydroxide at a red heat. Anhydrous sodium oxide (prepared by burning sodium in a mixture of air and oxygen, and continuing the combustion with excess of sodium to prevent the formation of sodium peroxide) acts very energetically on water, so that in the reaction $Na_2O + H_2O + Aq$, the development of heat is equivalent to 55·56 heat-units. Since, according to Berthelot, the amount of heat evolved by the combination of sodium hydroxide with water = 19·5 (for 2 mols.), then the amount of heat set free by the reaction $Na_2O + H_2O = 55 - 19{\cdot}5 = 35{\cdot}5$. Now, according to Thomsen, $Na_2 + O + Aq = 155{\cdot}2$ units, and therefore $Na_2 + O = 155{\cdot}2 - 55{\cdot}0 = 100{\cdot}2$, or 50·1 units, for each atom of sodium. From this it follows that the reaction $NaOH + Na = Na_2O + H$ is accompanied by an absorption of heat, thus:— $+ 50{\cdot}1 - (34{\cdot}5 + 17{\cdot}75) = - 2{\cdot}15$. If this be correct, then the inverse action $Na_2O + H = NaHO + Na$ must give rise to an evolution of heat. Experiment has

confirmed this conclusion, for sodium oxide is easily decomposed by hydrogen into sodium hydroxide and sodium. T. C.

Thermo-chemical Relation between the Boiling and Melting Points of Solid Elements. By H. F. Wiebe (*Deut. Chem. Ges. Ber.*, **12**, 788—791).—In a previous communication (*Ber.*, **11**, 610) the author pointed out a relation between the atomic volumes and coefficients of expansion of elements in the solid state, and he now gives a practical application of this relation. *For a series of bodies, the amount of heat, which at the ordinary atmospheric pressure is necessary to raise the temperature of equal volumes of the same body from the melting to the boiling point, bears a constant proportion to the reciprocal of the absolute coefficient of expansion.* The absolute coefficient of expansion =

$$\frac{\text{Specific gravity}}{\text{Atomic weight} \times \text{coefficient of expansion}}$$

If d = specific gravity; a = atomic weight; α = coefficient of expansion near the boiling point; c = specific heat (liquid water = 1); s = boiling point; σ = melting point; then $\frac{\frac{d}{a \,.\, \alpha}}{d \,.\, c \,.\, (s-\sigma)} = 2$, or

$$2 \,.\, a \,.\, \alpha \,.\, c(s-\sigma) = 1.$$

By the use of this formula, the boiling points of S, Se, P, and Hg have been calculated, and the results obtained agree very well with the experimental numbers. For other substances the melting and boiling points of which are known, the cubical expansion is wanting for high temperatures. In this case, by the use of the linear coefficient of expansion at 40° (β_{40}) the following formula may be employed:—

$$\frac{\frac{d}{\beta_{40} \, a}}{c \,.\, d \,.\, (s-\sigma)} = 9.$$

This formula is applied in the case of S, Se, Zn, and Cd also with very good results.

Note by Abstractor.—Williams and Carnelley (*Chem. Soc. J.*, 1879, Trans., 563) have recently shown that although the boiling point of Bi calculated by the above method agrees with experiment, yet in the case of Sn, Pb, Sb, and I, widely different results are obtained. T. C.

Dissociation of Chloral Hydrate. By A. Naumann (*Deut. Chem. Ges. Ber.*, **12**, 738—742).—The author proves the decomposition of chloral hydrate when distilled, by analysis of the distillate and the residue left in the retort. The estimation of the chlorine gives the amount of chloral in the residue and distillate, and from this the percentage of water may be calculated. In this way it is shown that the residue contains a larger percentage of water than the distillate. This result is in accordance with those of Engel and Moitessier (*Compt. rend.*, 1879, **88**, 275); and of E. Wiedemann and R. Schulze (*Ann. Chim. Phys.* [2], **6**, 293). P. P. B.

Proof of the Law of Multiple Proportion. By F. Kessler (*Ann. Chem. Phys.* [2], **6**, 460—463).—The oxidising value of potassium permanganate, and also that of manganese dioxide, obtained from the former by reduction to manganous oxide and precipitation with bromine-water in an alkaline solution, were determined. These values were found to be as 5 : 2, which is the proportion required by the formula of the two substances. Without a knowledge of atomic weights, and without making any weighings, a proof of the law of multiple proportion is thus obtained. M. M. P. M.

Inorganic Chemistry.

Sulpho-oxychlorides. By F. Clausnizer (*Liebig's Annalen*, **196**, 265—298).—The results of the experiments on the action of sulphuric monochloride on the chlorides of selenium, titanium, antimony, tin, and silicon, and the several methods for preparing sulpho-selenium oxytetrachloride and sulpho-titanium oxytetrachloride, which are described in this paper, have already been published (*Ber.*, **11**, 2007—2013, and this volume, 201).

Sulpho-selenium oxytetrachloride, $ClSO_2.OSeCl_3$, crystallises in white, silky needles, which decompose on exposure to the air, or when brought in contact with water, forming hydrochloric, sulphuric, and selenious acids. This substance is slightly attacked by concentrated sulphuric acid. It melts at 163°, and boils at 183° with dissociation.

Sulpho-titanium oxytetrachloride, $ClSO_2.OTiCl_3$, when dried at 100°, is an amorphous powder, soluble in water with evolution of chlorine and sulphurous anhydride. It fumes on exposure to damp air, and is converted into a white moist mass, which is no longer soluble in water.

The author finds the specific gravity of selenious oxide to be 3·9538, and that of selenious acid, 3·0066, compared with water at 15·3°. Sulphuric monochloride, $SO_2(OH)Cl$, boils at 150—151°, under a pressure of 726 mm.; the boiling point falls 1°, with a diminished pressure of 20·6 mm. W. C. W.

Sulphides of Phosphorus. By G. Ramme (*Deut. Chem. Ges. Ber.*, **12**, 940—941).—*Phosphorus pentasulphide* is obtained in pale yellow prisms, by heating in sealed tubes at 210° for 8 hours a solution of sulphur and common phosphorus in carbon bisulphide. Attempts to prepare the trisulphide P_2S_3 by this method, or by heating a mixture of amorphous phosphorus and sulphur, were unsuccessful; in each case the disulphide PS_2 was formed. *Phosphorus disulphide* crystallises in pale yellow transparent needles, which melt at 296—298°. The compound P_4S_3 could not be obtained, and the substance described by Berzelius as PS_{12}, proved to be crystals of sulphur, mixed with a small quantity of phosphorus. W. C. W.

Preparation of Barium from Barium Amalgam. By J. Donath (*Deut. Chem. Ges. Ber.*, **12**, 745—747).—The author finds

that the body prepared according to Crookes' method (*Jahresb.*, 1862, 126), from barium amalgam, and supposed to be barium, is a solid amalgam, containing as much as from 62—77 p. c. of mercury; and even when heated strongly in porcelain tubes this amalgam does not yield the metal. By this means, however, the author obtained some pellets, whose surface was bronze-coloured, which appears to be the true colour of barium (Bunsen and Matthiesen, *Jahresb.*, 1855, 323). The objection to Crookes' method applies also to Kern's method (*Jahresb.*, 1875, 198), of decomposing barium iodide with sodium, dissolving out the barium with mercury, and distilling. P. P. B.

New Determination of the Equivalent of Aluminium. By A. Terreil (*Bull. Soc. Chim.* [2], **31**, 153—154).—A known weight of aluminium was introduced into a combustion tube drawn out at both ends, and carbonic anhydride passed through the apparatus to expel air; dry hydrochloric acid gas was then substituted for the anhydride, while the tube was brought slowly to a red heat. The hydrogen which was disengaged was collected over water and measured. 0·41 gram of aluminium gave 508·2 c.c. of hydrogen at 0° and 760 mm. = 0·0455 gram of hydrogen. From this result the number 9·01 is calculated as the equivalent of aluminium.

The formula of the chloride will consequently be $AlCl_3$, or Al_2Cl_6, if 27·03 be taken as the atomic weight of aluminium. The chloride obtained was pulverulent and snow-white, but became yellow on exposure to air; its solution did not reduce gold salts in the same manner as do chromous and ferrous chlorides. J. W.

Potassium Ultramarine. By K. Heumann (*Deut. Chem. Ges. Ber.*, **12**, 784—788).—The property of silver ultramarine (*Ber.*, **10**, 1345), of undergoing double decomposition with the halogen compounds of other metals, renders the formation of a whole series of ultramarines possible. Potassium ultramarine is formed in this way when silver ultramarine is heated with excess of a halogen compound of potassium, best the iodide. The mass is afterwards treated with water, and the halogen compounds of silver extracted by ammonia. The analysis of the potassium compound thus obtained gave as follows:—

	K.	Al.	S.	Si.	O (by difference).
	25·19	13·84	7·14	15·40	38·43 = 100
Atomic proportions..	5·8	4·5	2·0	4·9	21·5

This shows that the atomic proportions are exactly the same as in the sodium and silver compounds, proving that the potassium and silver ultramarines are derived from the sodium compound by replacing the sodium in the latter by an equivalent of potassium or silver. Potassium ultramarine is a dark-blue, transparent, amorphous, homogeneous powder. When treated with dilute acids, it evolves one-half of its sulphur as sulphuretted hydrogen, whilst the other half is deposited in the free state. When digested at a gentle heat with a concentrated solution of silver nitrate, it passes quickly into yellow silver ultramarine. T. C.

Amalgams of Chromium, Iron, Manganese, Nickel, and Cobalt. By H. Moissan (*Bull. Soc. Chim.* [2], **31**, 149—151).—When a concentrated solution of chromous chloride is agitated with sodium amalgam, the mixture becomes heated, and there is produced by double decomposition sodium chloride and an amalgam of chromium. This amalgam is liquid, but less mobile than mercury; it decomposes slowly in dry air, but more rapidly in presence of moisture, becoming covered with a black coating of oxide. When it is heated above 350° in a current of hydrogen, the mercury volatilises, and metallic chromium is left, in the form of a black amorphous powder. The metal thus obtained is readily soluble in dilute sulphuric and nitric acids, but hydrochloric acid attacks it with difficulty, and only when heated; if ignited on platinum foil, it becomes suddenly incandescent, and is converted into green chromium sesquioxide.

Amalgams of manganese, iron, nickel, and cobalt may also be prepared in the manner above described, or (with the exception of iron) by decomposing a concentrated solution of their chlorides with an electric current, using a mercurial negative electrode; they contain for a given weight more of the metal amalgamated than the amalgam of chromium.

The metallic manganese obtained by the distillation of its amalgam, is pyrophoric: it decomposes water slowly at the ordinary temperature, but more quickly at 100°. J. W.

Artificial Production of Native Carburetted Iron. By S. Meunier (*Compt. rend.*, **88**, 924).—By passing carbonic oxide over a mixture of the chlorides of iron and nickel, contained in a porcelain tube heated to redness, a carburetted iron, rich in nickel, was obtained, in forms resembling in disposition and texture certain minerals found in Greenland and elsewhere. R. R.

Cuprous Chloride. By M. Rosenfeld (*Deut. Chem. Ges. Ber.*, **12**, 954—959).—Pure white cuprous chloride may be easily obtained, if the precipitate formed on passing sulphurous anhydride through a solution of copper sulphate and common salt is thoroughly washed with glacial acetic acid. When carefully dried, the cuprous chloride may be exposed to the air and to sunlight without changing colour.

On the addition of potassium dichromate to a solution of cuprous chloride in sodium thiosulphate a dark brown powder slowly separates out, which has the composition $CuCr_6O_{12} + 12H_2O$, or $CuCr_4O_9.Cr_2O_3 + 12H_2O$.

Potassium chromate produces in a solution of cuprous chloride in sodium chloride a black precipitate, which rapidly changes in colour to a yellowish green. It is soluble in acids, but insoluble in water. Its composition is $Cu_6Cr_3O_{12} + 9H_2O$. W. C. W.

A New Copper Nitrite. By B. van der Meulen (*Deut. Chem. Ges. Ber.*, **12**, 758—759).—This compound is prepared by heating a mixture of the aqueous solutions of copper sulphate and potassium nitrite with alcohol; potassium sulphate and a bluish-green precipitate of copper hydrate are produced, and the filtrate yields on evaporation

crystals of nitrite of the composition $Cu(NO_2)_2.3Cu(HO)_2$. It is stable at ordinary temperatures, sparingly soluble in water and alcohol, and dissolves in acids and ammonia, forming deep blue solutions. It is decomposed by continued boiling with water. Its formation is attended with that of ethyl nitrite. P. P. B.

Action of Light on Silver Chloride. By A. Riche (*J. Pharm.*, [4], **29**, 392—396).—D. Tommasi (*ibid.* [4], **29**, 293) states that by the action of sunlight on silver chloride suspended in water only a trace of hydrochloric acid goes into solution even when 9 grams of chloride are exposed, and, moreover, that the remaining chloride has the composition AgCl.

In answer to this, the author publishes results, obtained during the last 12 years, by exposing different weights of silver chloride, sealed with water in glass tubes, to the action of sunlight for periods varying from nine months to two years. These results show that silver chloride suspended in water, when exposed to the action of sunlight, is slowly decomposed, the solution becomes acid, and after a time chlorine is evolved. By constant agitation the reaction may be completed when the result is a chloride of silver, Ag_3Cl_2, and metallic silver, or a very unstable compound, which is decomposed by ammonia, yielding metallic silver: this remains to be determined. L. T. O'S.

Decomposition of the Haloïd Salts of Mercury, By E. Schaer (*Deut. Chem. Ges. Ber.*, **12**, 675—677).—A bottle of mercurous chloride kept in the same room with one of iodine was found to contain a considerable efflorescence of mercuric chloride and iodide. The presence of alkalis, or of bodies with an alkaline reaction, as well as the alkali and alkaline-earth metals, promotes the dissociation-changes, to which calomel and the corresponding green iodide are prone. This change of mercurous chloride, as well as of mercurous bromide and iodide into the higher compounds when in contact with soluble haloïd salts or with alkalis (contained in sugar, &c.), is of great importance from a medical point of view. G. T. A.

Mineralogical Chemistry.

The Spinelle of Tiriolo in Calabria. By F. Mauro (*Gazzetta chimica italiana*, **9**, 70—71). This variety of spinelle found at Monte de Tiriolo, near Catanzaro, is opaque, dark greenish-blue, feebly lustrous, and brittle with irregular fracture. Sp. gr. at 12° = 3·70. Its analysis gave the following results:—

Sb_2O_3.	Al_2O_3.	ZnO.	MgO.	FeO.
0·34	63·64	21·28	12·34	4·53

corresponding with the formula $(ZnMgFe)Al_2O_4$. C. E. G.

Chemical Composition of Triphylite. By S. L. Penfield (*Am. J. Sci.* [3], **17**, 226—229).—The author has analysed specimens of triphylite from different localities, and also a specimen of the allied lithiophilite, with the following results:—

(1.) Triphylite from Norwich, Mass. Colour greyish-green. Sp. gr. = 3·534:—

P_2O_5.	FeO.	MnO.	CaO.	MgO.	Li_2O.	Na_2O.	H_2O.
44·76	26·40	17·84	0·24	0·47	9·36	0·35	0·42

(2.) Triphylite from Bodenmais, Bavaria. Colour light blue. Sp. gr. = 3·549:—

P_2O_5.	FeO.	MnO.	CaO.	MgO.	Li_2O.	Na_2O.	K_2O.	Gangue.
43·18	36·21	8·96	0·10	0·83	8·15	0·26	0·87	0·83

(3.) Lithiophilite from Branchville, Conn. Colour light clove-brown. Sp. gr. = 3·482:—

P_2O_5.	FeO.	MnO.	Li_2O.	Na_2O.	H_2O.	Gangue.
45·22	13·01	32·02	9·26	0·29	0·17	0·29

These numbers correspond with the ratio 1 : 1 : 1 required by the general formula, $R''_3P_2O_8 + R'_3PO_4$, or $R''R'PO_4$.

The following series of analyses shows clearly the transition from triphylite, $LiFePO_4$, to lithiophilite, $LiMnPO_4$:—

	Triphylite.			Lithiophilite.	
	(1) Bodenmais.	(2) Norwich.	(3) Grafton.	(4) Branchville.	(5) Branchville.
P_2O_5 ..	43·18	44·76	44·03	45·22	44·67
FeO ..	36·21	26·40	26·23	13 01	4·02
MnO ..	8·96	17·84	18·21	32·02	40·86
CaO ..	0·10	0·24	0·94	—	—
MgO ..	0·83	0·47	0·59	—	—
Li_2O ..	8·15	9·36	8·79	9·26	8·63
K_2O ..	—	—	0·32	—	—
Na_2O ..	0·26	0·35	0·12	0·29	0·14
H_2O ..	0·87	0·42	1·47	0·17	0·82
Gangue	0·83	—	—	0·29	0·64
	99·39	99·84	100·70	100·26	99·78

C. H. B.

Distribution of Cerium, Lanthanum, and Didymium. By A. Cossa (*Gazzetta chimica italiana*, **9**, 118—140).—This exhaustive paper is divided into six sections. The first details the author's researches on those apatites which show the characteristic absorption-band of didymium when examined by the spectroscope. Fourteen specimens of apatite which gave this reaction are described; they varied greatly in colour and appearance, and were from various parts of the world. Analyses (details of the methods are given) of three of the apatites from Snarum in Norway, from Bamle in Norway, and from Canada, showed that cerium and lanthanum were present as well as didymium.

In the second section 14 apatites are mentioned, which, although

the didymium line could not be seen with the spectroscope, were found to contain the cerite metals (cerium, lanthanum, and didymium). From these results it would seem probable that the cerite metals are present in minute quantity in all apatites.

The third section is devoted to the results of the examination of calcareous minerals for the cerite metals. The only reagents employed were water, dilute nitric acid, ammonia, and oxalic acids, all of which were carefully tested to ascertain their purity; and every precaution was taken to exclude the possibility of the accidental introduction of traces of the cerite metals during the operations. The minerals examined were white crystalline Carrara marble, a shelly limestone from the province of Avellino, and a calcareous deposit, formed in a terra cotta tube of a Roman aqueduct, near Cividalo nel Friuli, all three of which were found to contain the cerite metals. These were also detected in bone-ash, such as is used for cupels, in the ashes of beechwood, and in minute traces in the ashes of rice. It is important to note in connection with the fact that the ashes of rice contain a much larger proportion of magnesium phosphate than of the calcium salt, that the author was unable to detect the presence of the cerium metals in wagnerite (magnesium phosphate).

In Section 4 the author gives the determination of the amount of cerite metals in scheelite (calcium tungstate). That of Traversella was found to contain on an average 0·22 per cent. of the mixed oxides of cerium, lanthanum, and didymium. The scheelite of Meymac (Corrèze) contained a much smaller quantity.

The fifth section treats of the artificial production of didymiferous scheelite and the preparation of crystallised didymium tungstate. Manross (*Annalen*, **81**, 243) obtained crystallised scheelite by fusing at a very high temperature a mixture of sodium tungstate with excess of calcium chloride. The author finds that it may be obtained more easily and in larger crystals by fusing a mixture of amorphous calcium tungstate with sodium chloride. If to this a small quantity of didymium tungstate is added, scheelite crystals are obtained, which appear perfectly transparent under the microscope, and exhibit the characteristic didymium-band when examined by the spectroscope, in the same way that the Traversella crystals do.

By a tedious series of fractional precipitations and crystallisations pure didymium oxide was obtained from the cerite of Bastnaes. Two analyses of the sulphate gave results which agree with the atomic weights proposed by Mendelejeff and by Marignac rather than with the more recent one of Clève. A moderately concentrated hot solution of pure didymium nitrate prepared from the oxide, when mixed with a hot solution of sodium tungstate, yields a pale rose-coloured gelatinous precipitate, which when dry has the formula $Di''WO_4$. This amorphous salt was heated with sodium chloride at a high temperature for four hours in a covered crucible; and on examining it when cold it was found that the sodium chloride had volatilised, and that the bottom of the crucible was covered with beautiful yellowish rose-coloured octohedral crystals of pure didymium tungstate. Apparently they belong to the dimetric system.

The sixth and last section gives a detailed description and measure-

ment of the absorption-spectra of some didymiferous minerals. Those examined were parisite from Santa Fe (New Granada), turnerite from the Grisons and the Vallais, the scheelite of Traversella, the apatites of Jumilla, of Cerro Mercado, and of Cabo di Gates, monazite from Arendal, the cerite of Bastnaes, and kischtimite from Borsowska in the Urals. C. E. G.

Presence of Chlorine in Scapolites. By F. D. Adams (*Am. J. Sci.* [3], **17**, 315—320).—With one exception no mention has been made of the presence of chlorine in minerals of the scapolite family. An analysis of a scapolite made by the author was deficient by several per cent. The powdered mineral when heated alone gave a heavy sublimate, the solution of which in water gave a precipitate with silver nitrate and also with barium chloride. The analysis of the sample was repeated, the chlorine being determined by fusing the mineral with sodium carbonate, and precipitating with silver nitrate. The sulphuric acid was also estimated. The numbers obtained were :—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.
54·859	22·448	0·486	9·092	trace	1·127	8·365

Cl.	SO_3.	H_2O (comb.).	H_2O (hygr.).	
2·411	0·796	0·141	0·722	= 100·447

Deduction for O replaced by Cl 0·59 = 99·857.

Excluding NaCl and Na_2SO_4 the ratio for basic elements and silica is 1 : 1·94.

The scapolite occurs in veins of varying width, associated with blackish mica, green hornblende, quartz, calcite, green apatite, and black tourmaline. It is found in somewhat large crystals, with cleavage parallel to the lateral faces, which are deeply striated. Sp. gr. 2·628.

Fourteen specimens of scapolites from different localities were examined, and were all found to contain chlorine in quantities varying from a trace to 2·4 per cent. In some cases this chlorine was not driven off, even on exposure to a white heat. It seems probable that when the scapolite decomposes, the chlorine is one of the first constituents to disappear. C. H. B.

Presence of Mercury in the Mineral Waters of Saint-Nectaire. By E. Willm (*Compt. rend.*, **88**, 1032—1033).—In 1877 Garrigou announced the detection of mercury in the spring of Rocher in Saint Nectaire-le-Haut (Puy-de-Dôme). In 1878 J. Lefort published a note, in which he failed to establish this result. The author has succeeded in detecting a trace of mercury in 9 litres of the water. This element, however, could not be found in the deposit left by the water, nor even in another sample from the same spring. It is also absent from the neighbouring spring of Mont-Cornedore. The author concludes that if mercury is really a constant constituent of the spring of Rocher, which he regards as doubtful, it is present only in extremely minute quantity. C. H. B.

Thermal Water of Termini Imerese. By E. Paternó and G. Mazzara (*Gazzetta chimica italiana*, **9**, 71—75).—Three analyses of this water were made by Furitano in the years 1818, 1823 (after the earthquake), and in 1825:—

	1818.	1823.	1825.
Free carbonic acid	0·282	0·1867	0·369
$CaCO_3$	0·456	0·318	0·477
$CaCl_2$	0·130	0·405	0·121
$MgCl_2$	1·823	0·897	1·745
NaCl	9·223	8·970	9·706
Na_2SO_4	0·325	0·296	0·214
$CaSO_4$	0·911	0·607	0·723
$MgSO_4$	—	0·339	0·163
Loss	0·153	0·766	0·239
	13·021	12·598	13·388

The water is colourless, inodorous, and has a saline and slightly bitter taste. Its temperature is constant at 43·5°, and its sp. gr. at 0° to water at 0° is 1·0119. A kilogram of the water contains—

N 13·32 c.c.	= 0·0168 gram.	NaCl	11·9358 gram.
O 0·76	= 0·0011	$CaCl_2$	0·0560
CO_2	0·1300	$MgCl_2$	1·3756
SO_4	1·1078	$CeSO_4$	1·5683
Cl	8·3072	$CaCO_3$	0·1210
Na	4·6027	$MgCO_3$	0·0066
Mg	0·3492	CO_2	0·0733
Ca	0·5291		

Traces of iodine and of lithium were detected in the residue obtained by the evaporation of 150 litres of the water. C. E. G.

Mineral Water of Rosheim in Alsace. By F. B. Power (*J. pr. Chem.* [2], **19**, 223—230).—Temperature of water = 11·2°. Temperature of air = 22·1°. Reaction neutral. Sp. gr. = 1·00018358.

Mineral Matter in 10,000 *parts by weight of Water.*

$BaSO_4$.	$CaSO_4$.	K_2SO_4.	Na_2SO_4.	$(NH_4)_2SO_4$.	$(NH_4)HCO_3$.
0·0011	0·0324	0·0445	0·0008	0·1552	0·0102

$CaH_2(CO_3)_2$.	$MgH_2(CO_3)_2$.	$FeH_2(CO_3)_2$.	NH_4Cl.	LiCl.	$MgCl_2$.
3·1792	0·5568	0·006	0·0677	0·0128	0·0478

$Mg(NO_3)_2$.	Al_2O_3.	SiO_2.	H_3PO_4.	Organic matter.	
0·1631	0·0019	0·1082	0·0048	trace	Total = 4·3925

Free CO_2.	O.	N.
0·6851	0·2198	0·5755

Percentage composition of gas escaping from the water = CO_2, 2·22, O, 13·92, N, 83·86.

An analysis of this water was made in 1836 by Coze, Persoz, and Jargeaud. The amount of lithium found by these chemists was about 12 times as great as that now found by the author. The older methods for estimating lithium were not trustworthy. M. M. P. M.

Waters of the Cheliff. By Balland (*J. Pharm.* [4], **29**, 405—408).—The River Cheliff rises in the neighbourhood of Tiaret, flows through Algeria, and empties itself into the Mediterranean Sea. Its course is about 400 kilometers, and during some months in the year its flow is very rapid, carrying along with it large quantities of sand and clay, which it deposits on standing.

The analysis of the water gave the following results per litre:—

Carbonic anhydride	0·13716 gram
Sulphuric ,,	0·17989 ,,
Hydrochloric acid	0·18436 ,,
Soda	0·18020 ,,
Potash	0·00500 ,,
Lime	0·09780 ,,
Magnesia	0·03800 ,,
Sesquioxide of iron	0·00150 ,,
Alumina	0·00300 ,,
Silica	0·01100 ,,

It does not contain copper, bromine, iodine, phosphoric, nitric, or boric acid.

The matter in suspension, which varies in quantity from 4 to 27 grams per litre, according to the rapidity of the river, consists chiefly of silica and clay, with a small quantity of iron, lime, and magnesia. L. T. O'S.

Organic Chemistry.

Eikosylene, a Derivative of Brown Coal Paraffin. By E. Lippmann and J. Hawliczek (*Wien Acad. Ber.* [2 Abth.], **78**, 251—258).—It is stated that almost all the paraffin in the market contains oxygen to some extent. A sample of ozokerite paraffin, for example, gave on analysis percentage numbers for C and H, adding to 98·78 instead of to 100. This oxygen was easily removed by heating with sodium at 250° in sealed tubes. The melting point of this paraffin was 63°. Some brown coal paraffin, repeatedly recrystallised from alcohol, left an insoluble portion, with a melting point 37°, which treatment with sodium did not alter.

Chlorination.—On heating the hydrocarbon with phosphorus pentachloride alone at 215°, carbonisation ensued, but when the paraffin was dissolved in carbon tetrachloride, and the necessary quantity of phos-

phorus pentachloride added, it could be heated to 215° without carbonisation. On opening the tubes there was always much pressure from formation of hydrochloric acid. In order to obtain larger quantities of the product the phosphorus pentachloride was placed apart in a small flask, connected with that containing the paraffin, which was heated up to 170°; by inclining the bulb or small flask containing the pentachloride, the necessary amount was gradually added. The product coming from the condenser was a mixture of phosphorus trichloride with oily chlorides, from which was isolated one having the composition $C_{20}H_{39}Cl$ (b. p. 225—230°). It is derived from $C_{20}H_{40}Cl_2$ by loss of HCl. By distillation, it loses HCl and yields $C_{20}H_{38}$. This body named eikosylene boils at 314—315° (uncorr.). Eikosylene absorbs chlorine and bromine readily, without evolution of hydrochloric acid, and yields $C_{20}H_{38}Cl_2$ the dichloride, and $C_{20}H_{38}Br_2$, the dibromide. Eikosylene is derived from the paraffin $C_{20}H_{42}$. It is homologous with cetylene, which also combines with two instead of four bromine atoms, the typical member of the series being *acetylene*.

W. S.

Action of Water on the Haloïd Compounds of Alcohol Radicles. By G. Niederist (*Liebig's Annalen*, **196**, 349—360).—Methyl, hexyl, and allyl iodides are converted into the corresponding alcohols by the action of water at 100°.

According to Limpricht (*Annalen*, **139**, 307), when benzyl chloride is heated at 190° with twice its volume of water, anthracene and benzyl ether are produced. The author finds that benzyl alcohol is formed if the benzyl chloride is heated at 100°, with a large excess of water. Ethylene bromide is completely converted into ethylene glycol by boiling with a large excess of water in a flask fitted with an upright condenser, but propylene bromide, under similar treatment, yields a mixture of propylene glycol and acetone.

By long continued boiling with water, amylene bromide (b. p. 67—70°) is converted into amylene oxide, $C_5H_{10}O$ (b. p. 95°).

W. C. W.

Nitration of Derivatives of the Paraffins. By P. Lauterbach (*Deut. Chem. Ges. Ber.*, **12**, 677).—Ethylidene chloride heated at 100° in a sealed tube with excess of nitric acid, yields dinitro-chlorethane. The nitration is effected by fuming nitric acid in the cold in about 14 days. Ethylene chloride treated with fuming nitric acid yields an oil of penetrating odour, which gives with alcoholic potash first a red and then a yellow precipitate. Isobutyric acid and pentachlorethane were apparently unaltered when similarly treated.

G. T. A.

Nitrobutylene. By L. Haitinger (*Wien Akad. Ber.*, **77** [ii], 428—442).—With most bodies of the aromatic series, a simple treatment with concentrated nitric acid is sufficient to convert them into a nitro derivative, whilst in the fatty series nitrites or nitrates are formed. As however, the tertiary alcohols of the fatty series resemble the phenols in many respects, an attempt was made to obtain nitro-derivatives from them.

When concentrated red nitric acid of sp. gr. 1·52 is allowed to drop into an excess of trimethyl carbinol, nitrobutylene, $C_4H_7.NO_2$, is obtained as a light yellow oil of pungent odour and burning taste. It is heavier than water, and nearly insoluble therein. It boils at 154—158°, with slight decomposition, but may be distilled in a vacuum. The yield is only 6—10 per cent. of the trimethyl carbinol. In this reaction, carbonic anhydride, nitric oxide, and a little butylene are set free, whilst the washings of the crude product contain from 20 to 30 per cent. of the butyl alcohol employed, together with some hydrocyanic acids.

Nascent hydrogen from various sources converts nitrobutylene into ammonia, only traces of an amine being formed. Two neutral substances were also obtained, one almost insoluble in water, the other difficultly soluble and apparently of alcoholic nature.

On heating nitrobutylene with water for 60 hours in sealed tubes at 100°, it was completely dissolved, without formation of gaseous products, the following reaction taking place: $C_4H_7NO_2 + H_2O = CO(CH_3)_2 + CH_3NO_2$, acetone and nitromethane being formed.

Sodium hydrate solution easily dissolves nitrobutylene, but on acidifying it separates out again apparently unchanged. Alcoholic soda however, produces a dense precipitate, preceded by a yellow coloration. This precipitate, when purified and dried, is a yellowish powder, showing under the microscope only traces of crystallisation.

Sodium-nitrobutylene, $C_4H_6Na.NO_2$, is easily soluble in water, and in aqueous alcohol, with difficulty in absolute alcohol. On quickly heating it, an explosion occurs, and a carbonaceous residue remains behind. The body also turns brown on keeping.

On adding bromine to nitrobutylene until the coloration produced is permanent, the derivative $C_4H_7Br_2NO_2$ is obtained. It is a heavy yellowish oil, with an odour more pungent than that of nitrobutylene, and can be distilled, although with slight decomposition. It has feeble acid properties.

Dry hydrochloric acid gas, in contact with nitrobutylene, causes the formation of ammonia, hydroxylamine, and carbonic anhydride, and in all probability of formic and hydroxybutyric acids and acetone.

Constitution.—Looking at the behaviour of nitrobutylene with water, sodium hydrate, and bromine, its constitution must be represented by $(CH_3)_2C:CH.NO_2$, or $(CH_3)(CH_2.NO_2)C:CH_2$. The reducing action already described makes the second formula least probable, but there is no proof as to which is the correct one. A further study of the reactions of the bromination products of this body is likely to clear up this subject, and this is in hand.

Formation from Butylene and Nitric Acid.—Concentrated nitric acid is treated with butylene to saturation. It is absorbed with considerable evolution of heat. The nitro-product is identical in properties with the nitrobutylene obtained from trimethyl carbinol and nitric acid. W. S.

Researches on Perbromination. By Ezweiler (*Deut. Chem. Ges. Ber.*, **12**, 678).—When dehydrated potassium ferrocyanide is decomposed by bromine at 250°, there is formed, in addition to a metallic bromide, a greyish powder insoluble in cold water, but taken up by hot water, with formation of cyanuric acid and hydrobromic acid. This body would seem to be a tricyanogen tribromide.

G. T. A.

Ferricyanides. By J. Schuler (*Wien Akad. Ber.*, **77** [ii], 592—602).—There are certain ferricyanides which form salts with the general formula $Fe_2C_{12}N_{12}M_2''R_2$. Derivatives are now described in which ferricyanic acid is combined with bivalent lead.

Barium Ferricyanide, $Fe_2(C_{12}N_{12})Ba_3 + 20H_2O$.—Obtained by oxidising barium ferrocyanide with lead peroxide. The salt forms large brown-red crystals. It is easily soluble in water, but is insoluble in alcohol. The crystals effloresce in warm or dry air, and become covered with an orange-yellow crust. After long exposure to light, this powdered crust no longer dissolves completely in water, a greenish powder together with some barium ferrocyanide remaining behind. In the solution, much undecomposed ferricyanide mixed with some ferrocyanide is found. On being heated to 100° the yellow powder turns green superficially, and dissolves in water almost entirely. This reaction signifies a loss of 14 mols. water.

Lead Ferricyanide, $Fe_2(C_{12}N_{12})Pb_3 + 4Aq$.—Obtained by saturating lead carbonate with hydroferricyanic acid. The salt crystallises in yellowish-brown plates. The crystals produce a bronze-like mark on an earthenware plate. They are soluble in water, with difficulty in alcohol. In the dark, the salt remains permanent, but when exposed to light, it suffers alteration both of colour and weight.

Lead Ferricyanide with Lead Nitrate, $Fe_2(C_{12}N_{12})Pb_3.N_2O_6Pb + 12Aq$. —Contrary to the statements of Gmelin and v. Zepharovich (*Gmelin's Handbuch*, Bd. 1, p. 396, *Wien Akad. Ber.*, **59**, [ii], 805), the author finds that the above compound separates from mixed solutions of potassium ferricyanide and lead nitrate, in small garnet-like crystals, the larger ones being almost black and with a glassy lustre. The aqueous mother-liquors from the above crystals are partially decomposed on evaporation, with liberation of hydrocyanic acid, and separation of a greyish-blue precipitate. A solution of the salt, when exposed to light, suffers slight decomposition, with separation of a light-blue precipitate, consisting of lead ferrocyanide with some Prussian blue. The salt is much more soluble in hot than in cold water. The crystals are permanent in the air when protected from light. At 100°, they lose 12·6 per cent. of their weight; with stronger heating, hydrocyanic acid is evolved, and the mass becomes incandescent.

From mixed solutions of lead nitrate and potassium ferricyanide some of the above double salt is first obtained, and by evaporating the mother-liquors, potassium nitrate and large tabular black crystals of lead-potassium ferricyanide. The following equations express these formations: $2Fe_2(C_{12}N_{12})K_6 + 6N_2O_6Pb = Fe_2(C_{12}N_{12})Pb_3N_2O_6Pb + Fe_2(C_{12}N_{12})Pb_2K_2 + 10(NO_3K)$ and also $Fe_2(C_{12}N_{12})K_6 + 4N_2O_6Pb = Fe_2(C_{12}N_{12})Pb_3N_2O_6Pb + 6(NO_3K)$.

As lead nitrate and potassium ferricyanide did not yield lead ferricyanide, lead acetate was substituted for the nitrate, but it was found that both salts crystallised separately.

Lead Ferricyanide with Lead Oxide, $Fe_2(C_{12}N_{12})Pb_3.Pb_3(OH)_6 + 11H_2O$. —Obtained by mixing concentrated solutions of lead potassium ferricyanide or lead ferricyanide and basic lead acetate. The solutions must be allowed to stand some time in a well-closed flask. The salt consists of almost black cubical crystals, yielding a yellow powder on pulverisation. Sparingly soluble in alcohol and water, but more easily in a hot solution of basic lead acetate, and easily in acetic acid. 11 mols. water are lost at 100°: it is not altered on exposure to light.

Lead-potassium Ferricyanide, $Fe_2(C_{12}N_{12})Pb_2K_2 + 6Aq$.—Obtained by the action of solutions of 1 mol. of potassium ferricyanide or 2 mols. potassium sulphate on 1 mol. of the compound of lead ferricyanide with lead oxide, $Fe_2(C_{12}N_{12})Pb_3N_2O_6Pb + Fe_2(C_{12}N_{12})K_6 = 2Fe_2(C_{12}N_{12})Pb_2K_2 + 2KNO_3$. Black, glassy, tabular crystals, appearing dark-red by transmitted light. 1 part of the salt requires for solution 4·75 parts of water at 16°. It is very little soluble in absolute alcohol, and loses its 6 mols. of water of crystallisation at 100°; and also by merely standing over sulphuric acid. The compound of lead ferricyanide with lead nitrate is again obtained by acting with a solution of lead potassium ferricyanide on one of lead nitrate—

$$Fe_2(C_{12}N_{12})Pb_2K_2 + 2PbN_2O_6 = Fe_2(C_{12}N_{12})Pb_3N_2O_6Pb + 2KNO_3.$$

Ammonium-lead Ferricyanide, $Fe_2(C_{12}N_{12})Pb_2(NH_4)_2 + 6Aq$.—Prepared like the potassium-lead ferricyanide. Black glassy tabular crystals, more soluble in hot than in cold water. The aqueous solution decomposes on evaporation or exposure to the air. The salt is with difficulty soluble in alcohol. All the water of crystallisation is lost at 100°, or on drying over sulphuric acid, the salt becoming anhydrous, and changing from yellow to a greenish colour. No analogous compounds could be obtained with sodium, lithium, or calcium.

W. S.

Limit of the Separation of Alcohol from Water by Distillation. By J. A. Le Bel (*Compt. rend.*, **88**, 912).—The strongest alcohol which could be obtained by repeated distillation from a spirit of 95 per cent. contained 96·5 per cent. of alcohol. When alcohol of 98·5 per cent. was distilled in the same apparatus, the water came over in the first portion of the distillate, which contained 97·4 per cent. alcohol, and the residue 99·3 per cent. This result may have been in some degree influenced by a small proportion of amylic alcohol, which was found to be present. The spirit used in these experiments had been obtained from Chablis wine, and the author remarks that the crude amylic alcohol he separated from it had by no means the disgusting odour of potato oil or that of beet molasses. He thinks his results prove that a notable proportion of amylic alcohol may be present in a wine without detracting from its good quality. R. R.

Di-isobutylamine. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **12**, 948—950).—Di-isobutylamine is formed by the action of alcoholic ammonia at 100° on isobutyl bromide. In order to obtain the base in

the pure state, *nitroso-di-isobutylene* is prepared, by heating on a water-bath the crystalline precipitate which is thrown down by the addition of potassium nitrite to crude di-isobutylamine hydrochloride. The nitroso-compound separates out as an oily liquid, which solidifies when cooled in a freezing mixture. It melts below 0°; boils at 213—216°. It is decomposed by gaseous hydrochloric acid, yielding di-isobutylamine hydrochloride. The pure base, obtained by the addition of potash to the hydrochloride, boils at 135—137°. Reimer gives 120—122° as the boiling point of di-isobutylamine.

Tri-isobutylamine, obtained as a bye-product in the preparation of di-isobutylamine, boils at 180—186°. W. C. W.

Bases Derived from Aldol-Ammonia. By A. Wurtz (*Compt. rend.*, **88**, 940—946).—Aldol is dissolved in ether, and ammonia gas passed into the solution at 0° as long as it is absorbed, when aldol-ammonia separates in a beautiful crystalline condition. This latter was distilled rapidly over a naked flame, in portions of not more than 50 grams at a time, in a current of ammonia gas. The fused mass became slightly coloured, disengaging at first ammonia and aqueous vapour; from 100° to 140° an aqueous liquid passed over; from 140° to 250° an oily layer collected in the receiver, together with a thick watery liquid, leaving in the retort an abundant black residue, soluble in dilute hydrochloric acid.

The proportion of crude oil obtained was (1) 23 grams from 110 grams of aldol-ammonia; (2) 42 grams from 160 grams; (3) 205 grams from 870 grams.

The oil was separated from the aqueous liquid by shaking it with ether, then taken up by dilute hydrochloric acid, and finally precipitated by potash, and dried.

On submitting the mixture of bases to fractional distillation in a vacuum, it was found to boil from 80° to 250°, under a pressure of 0·02 mm. The most volatile and most abundant base was *collidine*, $C_8H_{11}N$, boiling at 177—179° under 7·63 mm. Its density was 0·943 at 0°, and its chloroplatinate, upon which its identification mainly rested, was well defined. When the temperature has risen to 120°, the distillate becomes thicker and more coloured; the bases then contain oxygen. The least oxidised base appeared to be more stable than the others, and its boiling point after several distillations became fairly constant at 160° under 0·02 mm. pressure. Its composition corresponded with the formula $C_8H_{13}NO$, which was further confirmed by the analysis of its hydrochloride and hydrobromide: when heated to 250° in a closed tube, it is partly decomposed, and the product on distillation yields a base containing no oxygen, and more volatile than the original oxidised base; this new substance did not appear to be collidine; its boiling point was higher and its chloroplatinate was soluble in alcohol.

In the original distillation of the bases from aldol-ammonia, the portion boiling above 150° was fractionated at every 10°, but the mixture of bases could not be effectively separated; the existence of the base $C_8H_{15}NO_2$ was nevertheless fairly established, since it yielded a well-crystallised hydrochloride. It is easy to account for the formation of these substances by the action of heat on aldol-ammonia, thus—

$$2C_4H_8O_2 + NH_3 = C_8H_{11}N + 4H_2O,$$
$$2C_4H_8O_2 + NH_3 = C_8H_{13}NO + 3H_2O,$$
$$2C_4H_8O_2 + NH_3 = C_8H_{15}NO_2 + 2H_2O.$$

It is not certain, however, whether the oxygen exists as hydroxyl, for the action of phosphoric chloride upon these bodies gave a product which was unsuitable for further examination.

Notwithstanding the fact that the base containing the largest proportion of oxygen was found among the least volatile portions of the distillate, it sometimes happened that the products passing over at 200° contained but a small proportion of oxygen, whilst those which distilled at 250° were almost invariably free from oxygen. J. W.

Decomposition of Ammonium Formate by Heat. By R. Andreasch (*Deut. Chem. Ges. Ber.*, **12**, 973—975).—The author finds, contrary to the statements in the text-books, that when ammonium formate is heated to 180°, the chief product of the reaction is formamide, and that only traces of hydrocyanic acid are produced. W. C. W.

Addition-product of Acetic Acid with Bromine and Hydrochloric Acid. By C. Hell and O. Mühlhäuser (*Deut. Chem. Ges. Ber.*, **12**, 732—735).—By the action of hydrochloric acid gas on a mixture of bromine and acetic acid, a tolerably stable crystalline compound is formed, having the composition $(C_2H_4O_2Br_2)_4HCl$.

Absorption of hydrobromic and hydrochloric acids by acetic acid.—Acetic acid absorbs hydrobromic acid with great avidity and evolution of heat; the saturated solution at 11° contains 40·8 per cent. HBr, and approximates in composition to the formula $(C_2H_4O_2)_2HBr$. The absorption varies with the pressure and temperature. By passing air through this solution, two-thirds of the hydrobromic acid is removed.

Hydrochloric acid is also absorbed by acetic acid, and the saturated solution at 4° contains 21·4 per cent. HCl, the greater portion of which may be expelled by passing air through the solution.

P. P. B.

Addition-products of Acetic Acid with Bromine and Hydrobromic Acid. By C. Hell and O. Mühlhäuser (*Deut. Chem. Ges. Ber.*, **12**, 727—732).—These crystalline compounds, originally observed by Steiner (*Ber.*, **7**, 184), are formed by the action of bromine on acetic acid saturated with hydrobromic acid. The determinations of bromine and hydrobromic acid show that they alter in composition when placed over lime, the most stable one having the composition $(C_2H_4O_2.Br_2)_4HBr$. It is identical with the compound formerly described by the authors as having the composition $C_2H_4O_2.Br_2$, which is formed by the action of bromine on acetic acid in presence of carbon bisulphide, and in this case owes its formation to the presence of hydrobromic acid resulting from the action of the bromine on the acetic acid. P. P. B.

Action of Bromine on Acetic Acid. By C. Hell and O. Mühlhäuser (*Deut. Chem. Ges. Ber.*, **12**, 735—738).—By heating molecular weights of bromine and acetic acid in sealed tubes in a water-

bath, and determining the amounts of hydrobromic acid formed every eight hours, the following results were obtained:—

Time.	Appearance of contents of tubes.	Percentage of hydrobromic acid.
8 hours	Liquid and opaque.	0·41
16 ,,	,, ,,	1·12
24 ,,	,, ,,	2·38
34 ,,	Partially crystalline.	5·16
42 ,,	Completely solid. Crystalline.	8·01

These results show that the quantities of hydrobromic acid increase in a geometrical progression; and further, that with this increase the formation of the crystalline compound $(C_2H_4O_2.Br_2)_4HBr$ takes place. The presence of a small quantity of hydrobromic acid, or some compound which yields hydrobromic acid, accelerates the reaction. This acceleration is probably due to the formation of the above additive product, and the consequent approximation of the molecules of bromine and acetic acid. P. P. B.

Isomeride of Angelic Acid. By E. Duvillier (*Compt. rend.*, **88**, 913—915).—The products of the action of ethyl bromisovalerate on sodium ethylate in alcoholic solution, are sodium bromide, ethyl ethoxyisovalerate, and ethyl iso-angelate—

$$CHMe_2.CHBr.COOEt + NaOEt = CHMe_2.CH(OEt).COOEt + NaBr.$$
$$CHMe_2.CHBr.COOEt + NaOEt = CMe_2 : CH.COOEt + NaBr + EtHO.$$

The substances were boiled together for some hours with inverted condenser. Water was added to the residue, and the lighter supernatant liquid was separated, dried, and distilled. The portion passing over between 155° and 190° was collected and saponified by alcoholic potash. The acids were separated by neutralising the product with sulphuric acid, adding zinc sulphate, evaporating to dryness, and taking up the residue with alcohol, which dissolved the zinc iso-angelate and ethoxyisovalerate. The mixed organic acids obtained from the zinc salt, when submitted to a low temperature, deposited iso-angelic acid in anhydrous crystals. They are only sparingly soluble in water, but readily in alcohol or ether. R. R.

Action of Hydrocyanic and Hydrochloric Acids on Ethyl Methylacetocetate. By H. König (*Deut. Chem. Ges. Ber.*, **12**, 768—770).—According to Demarçay (*Ber.*, **9**, 962) oxypyrotartaric acid may be obtained by acting on ethyl acetoacetate with hydrocyanic and hydrochloric acids. Similarly from ethyl acetomethylacetate, $CH_3.CO.CHMe.COOEt$, the author has obtained oxyadipic acid. The reaction is as follows:—

$$CH_3.CO.CHMe.COOEt + HCN = CH_3.COH(CN).CHMe.COOEt.$$
$$CH_3.COH(CN).CHMe.COOEt + 2HCl + 2H_2O = CH_3.COH(COOH).CHMe.COOH + NH_4Cl + EtCl.$$

P. P. B.

Substituted Malonic Acids. By M. Conrad (*Deut. Chem. Ges. Ber.*, **12**, 749—753).—The author prepares malonic acid by neutralising an alcoholic solution of monochloracetic acid with soda, and heating it for some time with the equivalent quantity of potassium cyanide dissolved in a little water. The cyanacetic acid thus obtained is saponified with soda, and the malonic acid precipitated from the solution as calcium salt. Ethyl malonate is prepared by heating the calcium salt with a mixture of alcohol and sulphuric acid.

Ethyl malonate like ethyl acetoacetate contains two atoms of hydrogen replaceable by sodium, forming a compound in which the sodium may in turn be replaced by alcohol-radicles, giving rise to derivatives of the form $CHX(COOEt)_2$, and $CYX(COOEt)_2$. By the successive action of sodium and ethyl iodide on methyl malonate, ethyl ethomalonate, $CH(Et)(COOEt)_2$ has been obtained. It is a liquid (b. p. 111·5°) which yields an ethomalonic acid (m. p. 111·5°) on saponification. This acid, when heated at 160°, is resolved into carbonic and butyric acids, and is identical with the acid described by Wislicenus (*Annalen*, **165**, 93) and Markownikoff (*ibid.*, **182**, 332). By treating ethyl ethomalonate with sodium and ethyl iodide, ethyl diethomalonate $CEt_2(COOEt)_2$ is obtained; it is an oily liquid (b. p. 223°), which yields on saponification an acid (m. p. 112°) sparingly soluble in water: this is isomeric with pimelic acid. Ethyl benzylmalonate prepared from ethyl sodiummalonate and benzoic chloride, is an oil boiling at 203°. The benzylmalonic acid (m. p. 117°) obtained from it is easily soluble in water, and at 180° is resolved into carbonic anhydride and hydrocinnamic acid. By the action of chlorocarbonic ether on solid ethyl sodiummalonate, formyltricarbonic ether is obtained, which by saponifying yields the acid $CH(COOH)_3$, m. p. 129°. Further by the action of ethyl chloracetate on this sodium-derivative of malonic acid, ethenyl-bicarbonic ether, $COOEt.CH_2CH(COOEt)_2$ is obtained. It is an oily colourless liquid boiling at 275—280°, and yields a crystalline acid (m. p. 159°) easily soluble in water.

The sodium in ethyl sodiummalonate may be replaced by chlorine or bromine. P. P. B.

Citramalic Acid. By T. Morawski (*Wien Akad. Ber.*, **76** [ii], 670—682).—The acid was prepared from monochlorocitramalic acid by a modification of Carius' method of treating it with zinc and hydrochloric acid. As soon as the reduction is completed, the solution is neutralised with ammonia, mixed with alcohol and stirred vigorously, when zinc citramalate is deposited in the crystalline state; a further quantity may be obtained by concentration of the mother-liquors. The washed zinc salt in a finely divided state is then suspended in water, decomposed by hydrogen sulphide, and the clear solution evaporated. When left for some days over sulphuric acid, it yields fine large crystals of the acid, $C_5H_8O_5$ (m. p. 119°), which are somewhat hygroscopic.

Ammonium citramalate forms minute needles, but neither the normal nor the *hydrogen-sodium* salt could be obtained in the crystalline state. The *normal calcium* salt may be obtained in the amorphous state, and of the composition $C_5H_6CaO_5 + 2H_2O$, by precipitation from concen-

trated solution in the cold, and in the crystalline state, of the composition $C_5H_6CaO_5 + 3H_2O$, by adding calcium chloride to a dilute solution of the ammonium salt, and boiling; the *hydrogen-calcium* salt $(C_5H_7O_5)_2Ca + 5H_2O$, crystallises in minute flat needles. The *normal barium* salt, $C_5H_6BaO_5$, and the *normal magnesia* salt, $C_5H_6MgO_5 + 2H_2O$, are amorphous, but the *hydrogen-barium* salt $(C_5H_7O_5)_2Ba + 2H_2O$, is crystalline. The *zinc* salt, $C_5H_6ZnO_5 + 2H_2O$, and the *normal lead* salt, $C_5H_6PbO_5 + 3\frac{1}{2}H_2O$, are both crystalline; the *basic lead* salt, $C_5H_6PbO_5.PbO + 3H_2O$, is thrown down as a flocculent precipitate which becomes crystalline after a time. The *silver* salt, $C_5H_6Ag_2O_5$, is very stable, and crystallises from a hot solution in microscopic needles.

The citramalic acid prepared by the author differs in some respects from that obtained by Carius, which he attributes to the latter being impure. Pure citramalic acid decomposes almost entirely on distillation, leaving but little residue; whilst water and citraconic anhydride pass over. The characters of citramalic acid show that it is quite distinct from glutanic acid, itamalic acid, and Demarçay's oxypyrotartaric acid, for although the last-named yields citraconic acid on distillation, its salts are decomposed, with formation of acetonic acid when their solutions are boiled, which is not the case with the salts of citramalic acid. C. E. G.

Pyromeconic Acid. By H. Ost (*J. pr. Chem.* [2], **19**, 177—208) (see also *ibid.*, 34—36, and this vol., 307).—In the dry distillation of meconic acid, Stenhouse obtained, in addition to pyromeconic acid, a compound to which he gave the name of paracomenic acid: the author details experiments which show that this compound is ordinary comenic acid, and not a modification of that acid as supposed by Stenhouse.

Pyromeconic acid crystallises in large brilliant prisms, which are easily soluble in water and in alcohol, less soluble in ether and in chloroform: it is completely volatilised at 100° (b. p. 225°). *Nitrosodipyromeconic acid*, $C_5H_3(NO)O_3.C_5H_4O_3$, obtained by the action of nitrous acid, is an exceedingly unstable compound, from which again two acids may be obtained, called by the author respectively *oxypyrometazonic acid*, $C_5H_5NO_4$, and *pyromecazonic acid*, $C_5H_5NO_3$; the latter is isomeric with amidopyromeconic acid; both of these acids form double compounds with hydrochloric acid; they are regarded by the author as possibly analogous to the azo-compounds of the benzene series. Pyromeconic acid, as also the acids obtained from it, is monobasic, it also forms but one acetyl-derivative. Pyromeconic acid is easily oxidised by excess of alkalis even without warming, with production of formic acid.

All attempts to form an ethereal salt of pyromeconic acid led only to negative results. The author regards pyromeconic acid and its derivatives, although containing less than 6 atoms of carbon in the molecule, as closely associated with compounds of the benzene series.

The principal properties of the more important derivatives of pyromeconic acid described by the author are as follows:—

A. Salts of Pyromeconic Acid.—The *potassium salt*, $C_5H_3O_2.OK$, is

prepared by mixing excess of potash with a concentrated solution of the acid, if a somewhat dilute solution be employed, the acid is oxidised with formation of formic acid.

The normal sodium salt was not obtained, but the acid salt, or as it is termed by the author, *sodium dipyromeconate*, $C_5H_3O_2.ONa.C_5H_3O_2OH$, was obtained by mixing alcoholic solutions of soda and of pyromeconic acid. The *calcium* and *barium* normal and acid salts are described. The latter only are obtained by decomposing the carbonates of the metals by pyromeconic acid, also by adding a little ammonia to a solution containing pyromeconic acid and chloride of barium or calcium. If much ammonia be added to such a solution, the normal salts are precipitated. An *ammonium salt* of uncertain composition, and readily undergoing decomposition, with reproduction of free pyromeconic acid, is obtained by mixing alcoholic solutions of the acid and ammonia: if aqueous solutions be employed, and much ammonia added, pyromeconic acid alone crystallises out.

Acetyl pyromeconate, $C_5H_3O_2.OC_2H_3O$, is easily prepared by heating together pyromeconic acid and acetic chloride, and crystallising the product from absolute alcohol: it forms colourless prisms (m. p. 91°), easily soluble in water, alcohol, and chloroform.

Pyromeconic acid unites in but very small quantity with hydrochloric acid, when the latter is passed over the former; but if ethereal solutions of pyromeconic acid and phosphorus chloride be mixed, white needle-shaped crystals quickly separate, having the composition $C_5H_3O_2.OH.HCl$. This compound is decomposed into its constituents by alcohol or water, or slowly by moist air. The corresponding compound $(C_5H_3O_2.OH)_2H_2SO_4$, separates in the form of prismatic crystals from a mixture of one molecule of pyromeconic acid, in ethereal solution, with less than one molecule of sulphuric acid: if equal numbers of molecules be employed, needle-shaped crystals separate, having the composition $C_5H_3O_2.OH.H_2SO_4$.

B. Derivatives of Pyromeconic Acid containing Nitrogen.—*Nitropyromeconic acid*, $C_5H_2(NO_2)O_2.OH$, is obtained by adding 1 to $1\frac{1}{2}$ parts of concentrated nitric acid to 2 parts of pyromeconic acid dissolved in 6 parts of acetic acid: the action is violent. When crystallised from alcohol, nitropyromeconic acid appears as small well-formed yellow prisms, which are very slightly soluble in cold water, and are decomposed, with explosion, by boiling water; insoluble in ether, benzene, chloroform, and carbon bisulphide; absolute alcohol, acetone, or hot acetic acid are the best solvents for the nitro-acid. The sodium, potassium, barium, and calcium salts of nitropyromeconic acid are described: the acid is monobasic. By reducing this acid with tin and dilute hydrochloric acid, removing the tin as sulphide and evaporating, large rhombic crystals are obtained having the composition $C_5H_2(NH_2)O_2.OH.HCl + H_2O$. By adding ammonia to an aqueous solution of the double compound, *amidopyromeconic acid*,

$$C_5H_2(NH_2)O_2.OH,$$

separates out. When crystallised from hot water, it forms long colourless needles; it is easily decomposed by alkalis, but not by water.

Nitrosodipyromeconic acid, $C_5H_2(NO)O_2.OH.C_5H_3O_2.OH$, is obtained

by passing nitrous acid (prepared from arsenious oxide and nitric acid) into an ethereal solution of pyromeconic acid. Details of the process are given in the original paper. This compound is exceedingly unstable; in moist air it evolves hydrocyanic acid; it separates as a light yellow crystalline precipitate, but could not be recrystallised, as the liquids which dissolve it also decompose it. Excess of nitrous acid readily converts it into nitropyromeconic acid: on warming it with water, nitrous and hydrocyanic acids are evolved with carbonic anhydride and other gases, and a crystalline compound of tolerable stability separates, having the composition $C_5H_5NO_4.C_5H_4O_3$. If this compound be heated with chloroform, it is decomposed, pyromeconic acid goes into solution, and *oxypyromecazonic acid*, $C_5H_4NO_3.OH$, remains. This acid in its general character resembles pyromeconic acid; it is easily soluble in hot water, soluble in cold water and in alcohol, insoluble in ether and chloroform. It crystallises in needles with 1 mol. of crystalline water, occasionally with 2 mols., and in anhydrous short prisms.

This acid is readily decomposed by excess of alkali, and by oxidising agents generally: it is not attacked by hydrochloric acid.

The potassium and sodium normal and acid salts, the barium and the acid thallium salts of oxypyromecazonic acid, are described. This acid very readily combines directly with other acids, *e.g.*, hydrochloric acid. The compound $C_5H_4NO_3.OH.HCl$ is formed by dissolving oxypyromecazonic acid in concentrated hydrochloric acid, warming gently, and leaving it to cool: it is easily decomposed into its constituents by the action of water.

Pyromecazonic acid, $C_5H_4NO_2.OH$.—This isomeride of amidopyromeconic acid is produced by long-continued action of tin and hydrochloric acid, at a moderate temperature, upon the foregoing acid. After removing excess of tin, the liquid is evaporated, when a double compound of pyromecazonic acid and hydrochloric acid—

$$C_5H_4NO_2.OH.HCl—$$

crystallises out. This compound is decomposed by water, the solution is evaporated to dryness to drive off hydrochloric acid, and pure pyromecazonic acid is obtained by recrystallising the residue from hot water. Pyromecazonic acid is only very slightly soluble in cold water, almost insoluble in alcohol, and insoluble in ether: it may be partially sublimed unchanged. The salts of this acid are unstable, being easily decomposed by the oxygen of the air, with production of blue and violet-coloured bodies. It forms double compounds with acids, and in its general behaviour resembles oxypyromecazonic acid.

M. M. P. M.

Ethylidenedisulphuric Acid. By G. J. Guareschi (*Gazzetta chimica italiana*, **9**, 75—89).—This acid is formed by the action of potassium permanganate on thialdine or on thioaldehyde.

Ethylidenedisulphuric acid is obtained as a colourless dense syrup on decomposing a solution of the barium salt with sulphuric acid and evaporating. It is very soluble in water and in alcohol, and when heated decomposes and volatilises without leaving any residue. Its

salts crystallise well and are all soluble in water, but the potassium, sodium, barium, and calcium salts are almost insoluble in alcohol. *Potassium ethylidenedisulphate*, $C_2H_4(SO_3K)_2$.—10 grams of thialdine agitated with 45 grams of permanganate dissolved in a litre of water soon renders the solution colourless. The filtrate from the manganese dioxide is concentrated, treated with baryta-water in slight excess, and after removal of the excess of baryta by carbonic anhydride, it is again concentrated and mixed with alcohol. The potassium salt is at once thrown down in the crystalline state, and may be purified by repeated solution in water and reprecipitation with alcohol. As thus obtained, it forms long prismatic plates very soluble in water. A hydrated salt, $C_2H_4(SO_3K)_2 + 2H_2O$, may be obtained in large transparent prismatic crystals, by allowing an aqueous solution of the salt to evaporate slowly. When heated, it burns with a blue flame, and gives off sulphurous anhydride, leaving a residue of carbonate and sulphide. Heated with sulphuric acid, it evolves sulphurous anhydride. It is not oxidised by potasssium permanganate, nitric acid, or chromic mixture. *Barium ethylidenedisulphate*, $C_2H_4(SO_3)_2Ba + 3\frac{1}{2}H_2O$. 10 grams of thialdine are oxidised by 30—35 grams of zinc permanganate in 300 c.c. water. The colourless acid filtrate treated with baryta-water in excess, and carbonic acid as above described, is concentrated and mixed with alcohol. The barium salt is then deposited in long colourless silky needles, whilst barium acetate remains in solution. A salt containing $3H_2O$ may be obtained in beautiful shining plates by evaporation of the aqueous solution. It loses $2H_2O$ at 100°, and the third molecule of water at 160—165°. *Sodium ethylidenedisulphate*, $C_2H_4(SO_3Na)_2 + H_2O$, prepared from the free acid by neutralising it with sodium carbonate, concentrating, and precipitating with alcohol, forms long silky plates. The *calcium* salt, $C_2H_4(SO_3)_2Ca$, obtained by a similar process, is crystalline and almost insoluble in alcohol. The *magnesium salt*, $C_2H_4(SO_3)_2Mg + 5H_2O$, the *cadmium* salt, $C_2H_4(SO_3)_2Cd + 2H_2O$, and the *copper* salt, $C_2H_4(SO_3)_2Cu + xH_2O$, were obtained by decomposing the sulphates of the metals with barium ethylidenedisulphate and evaporating the solutions; they are all crystalline and easily soluble both in water and in alcohol. The *zinc* salt is deliquescent and crystallises with difficulty.

The author assigns the formula $CH_3.CH(SO_2.OH)_2$ to ethylidenedisulphuric acid, and thialdine therefore would contain the group $CH_3.CH<\begin{matrix}S\\S\end{matrix}$, in which the two sulphur-atoms are united with the same carbon atom. This would seem to confirm the correctness of the formula $CH_3.CH<\begin{matrix}S.CH(CH_3)\\S.CH(CH_3)\end{matrix}>NH$, proposed by Erlenmeyer for thialdine.

When thioaldehyde is treated with potassium permanganate in the same way as thialdine, it also yields potassium acetate, sulphuric acid, and potassium ethylidenedisulphate. In the mother-liquors from which the last-mentioned salt has been deposited however, there remains a more soluble potassium salt, which crystallises with difficulty, and is precipitated by alcohol in an oily state. It has the properties of a thio-acid. Besides this, another highly sulphurised com-

pound is produced which crystallises readily from boiling water. A substance similar to this is formed in larger quantity when zinc permanganate is employed instead of the potassium salt. The author is engaged in investigating these compounds.

Ethylenedisulphuric acid.—This acid has been obtained in various ways by different chemists: the author employed a modification of Bender's method (*Annalen*, **148**, 96), and prepared it by boiling ethylene dibromide with a saturated solution of ammonium sulphite for six or seven hours. The product was boiled with excess of barium hydrate until ammonia was no longer evolved, and the barium ethylenedisulphate was separated by evaporation and precipitation with alcohol. It was purified by several resolutions in water and precipitations with alcohol. The *barium* salt, $C_2H_4(SO_3)_2Ba$, is anhydrous, and crystallises in slender needles; it is very much less soluble in water than the corresponding ethylidenedisulphate. The *potassium* salt, $C_2H_4(SO_3K)_2$, is also anhydrous, and crystallises in needles. From a consideration of the properties of these salts it is evident that ethylenedisulphuric acid and ethylidenedisulphuric acid are isomeric and not identical.

C. E. G.

Angelylthiocarbimide. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, **12**, 990—993).—In order to prepare angelylthiocarbimide, amylenebromide was digested with alcoholic ammonia, the product decomposed by potash and distilled. That portion of the distillate which boiled below 120°, and which contained *angelylamine*, was converted into the thiocarbimide by treatment with carbon bisulphide (*Ber.*, **7**, 511). Angelylthiocarbimide (b. p. 190°) is converted into the beautifully crystalline thiocarbamide (m. p. 103°) by the action of strong aqueous ammonia.

Crotonylamine boils between 75° and 80°, and resembles allylamine in its properties. The author intends to prepare methylcrotonylamine, $NHMe.C_4H_7$, in order to ascertain whether it is identical with piperidine.

W. C. W.

Nitrosothiohydantoïn. By R. Maly (*Deut. Chem. Ges. Ber.*, **12**, 967—973).—*Nitrosothiohydantoïn*, $C_3N_2H_3.(NO)OS$, is prepared by the action of nitric acid, sp. gr. 1·2, on thiohydantoïn, or by passing nitrous anhydride through a mixture of thiohydantoïn and water. The compound separates out as a yellowish crystalline meal, and may be obtained in microscopic pyramids by recrystallisation from a large quantity of boiling water. The crystals are insoluble in alcohol, ether, carbon bisulphide, and hydrocarbons. When one molecule of nitrosothiohydantoïn is dissolved in one equivalent of an alkali, a red solution is produced, but if two equivalents of the alkali are used, the solution has a yellow colour, which turns red on the addition of an acid.

On the addition of barium chloride to a solution of nitrosothiohydantoïn in ammonia, glistening yellow hexagonal and rhombic plates separate out, which have the composition,

$$C_3H_3(NO)N_2SO.BaH_2O_2 + H_2O.$$

This compound is very slightly soluble in cold water, and is partly decomposed by recrystallisation from hot water.

On the addition of an acid, it yields a red barium compound, which is soluble in water, but has not yet been obtained in the pure state. The red solution gives with lead acetate a yellowish-red precipitate; with zinc chloride, and with mercuric chloride, orange; and with silver nitrate, dark red precipitates.

The compound, $C_3H_2(NO)AgN_2SO.Ag_2O$, separates out as a dark reddish-brown precipitate, when silver nitrate is added to a solution of nitrosothiohydantoïn in ammonia which has been rendered slightly acid with acetic acid. A similar compound is formed with ferrous salts.

Attempts to prepare nitrosothiohydantoïc acid proved unsuccessful.

W. C. W.

Amides of Tertiary Hydrocarbon Radicles. By Rudneff (*Deut. Chem. Ges. Ber.*, **12**, 1023).—*Trimethylcarbinamine* is a mobile liquid, sp. gr. at 0° = 0·7137, at 15° = 0·6931, which boils at 44·5°. It forms crystalline salts with sulphuric, nitric, hydriodic, and thiocarbamic acids, and with platinum chloride.

Tertiary butylthiocarbimide boils at 142·5°, and crystallises in large plates, which melt at 10·5°, and have at 15° the sp. gr. 0·9187.

The *thiocarbamide*, $CS(NH.C_4H_9)NH_2$, forms large prisms, which melt at 165° with decomposition.

Dibutylthiocarbamide crystallises in colourless needles, which melt at 163°.

Tertiary amylthiocarbimide boils at 166°, and remains liquid at −10°.

W. C. W.

Durene Derivatives (α-Tetramethylbenzene). By Friedel, Crafts, and Ador (*Compt. rend.*, **88**, 880—884).—By the action of benzoic chloride on durene (α-tetramethylbenzene) in presence of aluminium chloride, the authors obtained a ketone, $C_6HMe_4.CO.Ph$, which they propose to call *phenyl-duryl-carbonyl*, indicating by the name *duryl* the residue C_6HMe_4. This ketone, treated at its boiling point with fused potash, splits up into benzoic acid and durene, yielding neither benzene nor any appreciable quantities of the acids, $C_6Me_4(COOH)_2$, or $C_6Me_4Bz.COOH$. The action of a mixture of sulphuric and nitric acids gave rise to a nitro-compound, but no oxidation. A brisk reaction occurred with bromine as follows—

$$C_6HMe_4.CO.Ph + 2Br = C_6HMeBr + Ph.CO.Br.$$

Reduction by hydriodic acid and phosphorus in a sealed tube at 240° for nine hours effected the replacement of the oxygen by H_2, giving rise to the compound $C_6HMe_4.CH_2Ph$, which crystallises in needles (m. p. 60·5°, b. p. 310°).

Two other substances are formed at the same time, one of which, after treatment with sodium, melts at 85°, and the other at 120°.

The ketone is very soluble in hot alcohol, from which it separates on cooling in acicular crystals. Another compound, formed at the same time as the above-mentioned ketone, is obtained in minute prisms (m. p. 269—270°) almost insoluble in boiling alcohol, but soluble in benzene. This substance is the diketone, $C_6Me_4(CO.Ph)_2$, which may be called *durenyl-dicarbonyl-diphenyl*, or *durenyl-dibenzoyl*, the name

durenyl indicating the residue C_6Me_4. This substance is easily obtained by treating phenyl-duryl-carbonyl with benzoic chloride and aluminium chloride at 150°. R. R.

Action of Copper on Trichlorobenzene. By HANHART (*Deut. Chem. Ges. Ber.*, **12**, 681).—When trichlorobenzene is gently heated with copper powder, a violent reaction takes place, and a crystalline body is formed, which is being investigated. G. T. A.

Action of Basic Compounds on Solutions of α-Dinitrochlorobenzene in Carbon Bisulphide. By C. WILLGERODT (*Deut. Chem. Ges. Ber.*, **12**, 768).—On treating a solution of α-dinitrochlorobenzene in carbon bisulphide with a certain quantity of alcoholic potash, yellow needles separate out (m.p. 193°), which appear to be metadinitrophenol sulphide (Beilstein and Kurbatow, *Ber.* **10**, 1992, and **11**, 2056). Further the author is engaged with the investigation of the bodies formed by the action of alcoholic or aqueous solutions of ammonia, aniline, toluidine, &c., on α-dinitrochlorobenzene dissolved in carbon bisulphide. P. P. B.

Action of Chloroform and Perchloromethane on Dimethyl-Aniline. By HANHART (*Deut. Chem. Ges. Ber.*, **12**, 680).—The product obtained by the action of chloroform and perchloromethane on dimethyl-aniline (*Ber.* **10**, 1205) is paramethylenedidimethylaniline, $CH_2(C_6H_4.NMe_2)_2$. The methylene base yields a large quantity of quinone on oxidation. G. T. A.

Desulphurisation of Dithiodidimethylaniline. By HANIMANN and HANHART (*Deut. Chem. Ges. Ber.*, **12**, 681).—When dithiodidimethylaniline (*Ber.*, **10**, 403), is treated with an ammoniacal solution of silver, or even with a solution of iron chloride, the sulphur is removed, and dioxydidimethylaniline, $NMe_2.C_6H_4.O.O.C_6H_4.NMe_2$, is formed. It is distinctly basic, crystalline, and melts at 90·4°. G. T. A.

Amylidene-aniline. By E. LIPPMANN and W. STRECKER (*Wien Akad. Ber.* [2 Abth.], **78**, 247—250).—By the action of valeraldehyde on aniline at 100°, Schiff obtained diamylidenediphenyldiamine, $(C_5H_{10})_2(C_6H_5)_2N_2$, a bitter yellow oil, combining neither with acids nor with platinum tetrachloride. By causing aniline gradually to act on valeraldehyde heat was generated, and a crystalline compound obtained, melting at 97°, and slightly decomposing. The body is indifferent to chloride of lime solution. On heating it with water, aniline is formed. This base yields triclinic crystals, and has the formula $(C_6H_5)(C_5H_{10})''N$, being evidently a tertiary aniline, for with HCl it forms a crystalline hydrochloride, consisting of $(C_6H_5)(C_5H_{10})''N.HCl$, and yielding a platinum double salt, $[(C_6H_5)(C_5H_{10})''H.HCl]_2 + PtCl_4$. Amylidene-aniline is the first example of a new series of tertiary bases, in which in 1 mol. of the amine, both hydrogen-atoms are replaced by the bivalent aldehyde residue. W. S.

Aniline Residues. By C. Hell and P. Schoop (*Deut. Chem. Ges. Ber.*, **12**, 723—727).—The solid body which separates out from high-boiling aniline residues is paratolylenediamine, which by distillation in a current of hydrogen, and crystallisation from water or alcohol, is obtained in thick shining prisms (m. p. 99°, b. p. 283—285°). The hydrochloride of this base crystallises in needles, which become brown on exposure to the air; with platinum chloride, it forms a double salt, easily soluble in water, and from which it crystallises in yellow leaflets. The sulphate is obtained as a white crystalline powder. Diacetyl-paratolylenediamine, $C_5H_3(CH_3)(NH\bar{A}c)_2$, crystallises from water in tufts of needles; it melts at 223°, and is identical with the compound described by Koch (*Annalen*, **153**, 132), and by Tiemann (*Ber.*, **3**, 8).

The liquid portion of the aniline residues, when distilled in a current of hydrogen, passes over at 280—285°, and forms a yellow oil, which on standing yielded a further quantity of the solid paratolylenediamine. The remaining liquid was converted into acetyl-derivatives; by crystallisation from water, these were separated into diacetyltolylenediamine and a very sparingly soluble acetyl-derivative which melts at about 290°, blackening and subliming at the same time. This acetyl derivative when distilled with soda yields paratolylenediamine. No conclusions can be drawn from the analysis of this acetyl-compound, which appears to be a derivative of paratolylenediamine. A further quantity of this substance is obtained by extracting with alcoholic ether the resinous mass left by evaporation of the aqueous mother-liquor. After extracting with ether, a resinous mass is left, which on distillation yields a bright reddish liquid, solidifying to a vitreous mass; it is easily soluble in water and alcohol, sparingly in ether, and on exposure to the air becomes green, and finally blackish-brown. Its composition is that of a diacetyltolylenediamine. By distilling with caustic soda, it yields a basic, uncrystallisable oil, boiling at 283—285°; its composition is approximately that of tolylenediamine, $C_7H_{10}N_2$.

This investigation shows that the principal constituent of these aniline residues is tolylenediamine, whereas those examined by Hofmann (*Ber.*, **4**, 812) consisted chiefly of phenylenediamine and some tolylenediamine, a difference due to the origin of the aniline oil.

P. P. B.

Orthotolylenediamine Derivatives. By A. Ladenburg and L. Rügheimer (*Deut. Chem. Ges. Ber.*, **12**, 951—954).—*Benzenylortho-tolylenediamine*, $Me.C_6H_3\begin{matrix}N\\ \diagup\\ \diagdown\\ NH\end{matrix}\!\!>C.Ph$. A flask containing a mixture of orthotolylenediamine and acetophenone in molecular proportions is gradually heated in an oil-bath until the thermometer indicates 180°; it is then maintained at this temperature for 36 hours. Small quantities of acetophenone are dropped into the flask from time to time in order to replace loss by volatilisation. The following reaction is supposed to take place, $Me.C_6H_3(NH_2)_2 + Ph.CO.CH_3 = Me.C_6H_3 : N_2HC\,Ph + H_2O + CH_4$. The contents of the flask are extracted with hot dilute hydrochloric acid; the acid solution on cooling deposits colourless needle-shaped crystals of the hydrochloride of

benzenylorthotolylenediamine. The free base melts at 240°, and is identical in its properties with the anhydro-base discovered by Hübner and Kelbe (*Ber.*, **8**, 875), and described by C. Meyer (*Dissertation*, Hanover, 1878).

The formation of *ethenyltolylenediamine*, $Me.C_6H_3\langle \overset{N}{\underset{NH}{}} \rangle C.Me$, takes place in two stages. When ethyl acetoacetate and orthotolylenediamine are brought together in the proportion of their molecular weights, the temperature of the mixture sinks whilst the diamine dissolves; the temperature then rises, water separates out, and the mixture solidifies to a crystalline mass, having the composition $C_{13}H_{18}N_2O_2$. The crystals melt at 82°, and are insoluble in water, but dissolve readily in other solvents.

The reaction which takes place is the following: $Me.C_6H_3(NH_2)_2 + Me.CO.CH_2.COOEt = Me.C_6H_3 : (NH)_2 : CMe.CH_2.COOEt + H_2O$. When this compound is heated at 116° it splits up into ethyl acetate and ethenyltolylenediamine (m. p. 198—199°).

$$Me.C_6H_3\langle \overset{NH}{\underset{NH}{}} \rangle CMe.CH_2.COOEt = Me.C_6H_3\langle \overset{N}{\underset{NH}{}} \rangle C.Me + Me.COOEt.$$

W. C. W.

A New Base, $C_{19}H_{16}N_2$. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **12**, 975—979).—The author finds that the true melting point of the base, $C_{19}H_{16}N_2$, which he first stated to be 67° (*Ber.*, **11**, 276), and afterwards 124° (*Ber.*, **11**, 840°), is really 75—78°. W. C. W.

Dibenzanilides. By Higgin (*Deut. Chem. Ges. Ber.*, **12**, 678—679). Two dibenzanilides are known, one obtained by Gerhardt and Chiozza (*Annalen*, **87**, 302), by heating benzanilide with benzoic chloride, the other by Losanitsch (*Ber.*, **6**, 176), from benzoic acid and phenylthiocarbimide. These are essentially different in properties, melting at 137° and 155° respectively. The author has prepared these anilides and analysed them. Both of them split up by the action of hydrochloric acid under pressure into aniline and benzoic acid. A new substance, apparently a third dibenzoyl-aniline, is obtained by heating benzanilide and benzoic chloride with zinc chloride. It is decomposed at a high temperature by hydrochloric acid into benzoic acid and a solid easily crystallisable base, which appears to be benzoylaniline.

A mixture of phenylthiocarbimide with benzoic acid when heated for some time to over 200°, no longer yields Losanitsch's dibenzanilide, but a basic body not yet investigated. G. T. A.

Preparation of Ethers of α-Dinitrophenol from α-Dinitrochlorobenzene. By C. Willgerodt (*Deut. Chem. Ges. Ber.*, **12**, 762—767).—These ethers may be prepared by dissolving α-dinitrochlorobenzene in the alcohol, and adding a solution of potash in the same alcohol. The reaction which takes place may be expressed thus: $C_6H_3(NO_2)_2Cl + KHO + HO.C_nH_{2n+1} = C_6H_3(NO_2)_2O.C_nH_{2n+1}$

+ KCl + H_2O. Thus by acting on α-dinitrochlorobenzene dissolved in methyl alcohol with a methyl alcohol solution of potash, α-dinitroanisol, $C_6H_3(NO_2).OMe$, is obtained. It is also formed by the action of a methyl alcohol solution of potash on an ethereal solution of the dinitro-compound; further the reaction takes place in presence of water. The ether crystallises in long yellow needles (m. p. 86—87°).

α-dinitrophenetol, $K_6H_3(NO_2).{}_2OEt$, has been prepared in a similar manner, substituting ethyl for methyl alcohol. It crystallises in long white needles (m. p. 86°). The corresponding propyl and amyl ethers have also been prepared, and are yellowish oily liquids.

α-dinitrophenylallyl ether, obtained by acting on α-dinitrochlorobenzene, dissolved in allyl alcohol with an alcoholic solution of potash diluted with water, crystallises in long needles or asbestos-like masses (m. p. 46—47°).

The glycerol ether, $C_6H_3(NO_2)_2.OC_3H_5(OH)_2$, is obtained by dissolving dinitrochlorobenzene in glycerol by the aid of heat, and adding to it a solution of potash in glycerol. The product may be crystallised from water, alcohol, or ether; from the latter it separates out as a crystalline mass, melting at 83°.

α-dinitrophenylphenyl ether, $C_6H_3(NO_2)_2.OPh$, is obtained by acting on a solution of α-dinitrochlorobenzene in carbon bisulphide with potassium phenylate. Crystallised from alcohol it forms long prisms or needles resembling urea crystals. It melts at 71°. Maikopar (*Ber.*, **6**, 564) obtained an ether, melting at 65°, by the action of potash on an alcoholic solution of phenol and dinitrochlorobenzene. This the author concludes to have been impure, since he has obtained an ether (m. p. 71°) by acting on an alcoholic solution of dinitrochlorobenzene with the calculated quantity of potassium phenylate. P. P. B.

Action of Soda-solution on Picramic Acid. By E. Trümpler (*Deut. Chem. Ges. Ber.*, **12**, 681).—When dinitroamidophenol is boiled with strong soda solution, a copious evolution of ammonia takes place and a crystalline body is formed, which is being investigated.

G. T. A.

Tribromophenol Bromide and Tribromoresorcinol Bromide. By R. Benedikt (*Deut. Chem. Ges. Ber.*, **12**, 1005—1006).—*Tribromophenol bromide*, $C_6Br_3H_2.OBr$, is produced when tribromophenol is acted on by an excess of bromine water. Boiling with alcohol, or reduction with tin and hydrochloric acid, converts this compound into tribromophenol.

The author considers it probable that Stenhouse's pentabromoresorcinol is a tribromoresorcinol bromide, $C_6HBr_3(OBr)_2$.

W. C. W.

Preparation of Trinitroresorcinol and Trinitro-orcinol. By V. Merz and G. Zetter (*Deut. Chem. Ges. Ber.*, **12**, 681).—Resorcinol is converted into a sulphonic acid by heating it with excess of sulphuric acid at 100°, and to this when cold are added successively slightly diluted, concentrated, and finally fuming nitric acid in excess. After a time, the product of the reaction is poured into cold water, when

the nearly pure nitro-derivative is thrown down. Trinitro-orcinol may be obtained by a similar process. G. T. A.

Action of Acetic Anhydride and Sodium Acetate on Quinone. By Sarauw (*Deut. Chem. Ges. Ber.*, **12**, 680).—By this reaction the author was in hopes of obtaining an acid of the formula

$$C_6H_4 : C_2(H.COOH)_2,$$

but found that it gave rise to diacetylquinol and dark tarry matter. By the action of bromine in excess on quinone dissolved in hot glacial acetic acid, it is converted into tetrabromoquinone. G. T. A.

Action of Ammonia on Quinones. By E. v. Sommaruga (*Deut. Chem. Ges. Ber.*, **12**, 979—982).—When phenanthraquinone is heated in sealed tubes at 100°, with strong alcoholic ammonia, a small quantity of a yellowish-brown resin and two crystalline compounds are formed. The green and brown bodies described by Anschütz and Schultz (*Annalen*, **196**, 51) were not observed. Two colourless crystalline compounds and a red crystalline colouring matter are formed by the action of alcoholic ammonia on dioxyindole. W. C. W.

Azophenols. By P. Weselsky and R. Benedikt (*Liebig's Annalen*, **196**, 339—349).—*Para-azophenol* can be prepared by fusing paranitrophenol with potash, and adding dilute sulphuric acid to the aqueous solution of the fused mass. The yellow scum which separates out is dissolved in ether, and recrystallised from alcohol. Para-azophenol may also be obtained by adding potassium phenylate to a solution of diazophenol nitrate,

$$HO.C_6H_4.N : N.NO_3 + C_6H_5.OK = HO.C_6H_4.N : N.C_6H_4.OH + KNO_3.$$

After the mixture has remained at rest for 24 hours, it is acidified with sulphuric acid, when a dark red crystalline precipitate separates out. This is washed with dilute soda, and the azophenol extracted with ether.

Para-azophenol forms reddish-brown, needle-shaped, triclinic crystals, which melt at 204°, with decomposition. It is soluble in alcohol, ether, and benzene, and forms a yellow crystalline barium derivative, containing 4 mols. water. It unites with bromine, yielding *tetrabromo-para-azophenol*, $C_{12}H_6Br_4N_2O_2$, which is deposited from benzene in golden-yellow needles. On fusing the bromine compound with potash, a prussian blue coloured mass is obtained, which turns violet and red on exposure to the air.

Ortho-azophenol may be prepared in a manner similar to that employed for the para-compound. It crystallises in golden scales, which melt at 171°, and are volatile without decomposition. The compound is insoluble in water, but dissolves freely in ether and in hot alcohol.

The barium and lead compounds have a red colour. The tetrabromo-derivative crystallises in dark yellow needles, possessing a metallic lustre. On fusion with potash, a reddish-violet colour is produced.

The authors have not yet succeeded in preparing metazophenol.

W. C. W.

Chemical Nature of the Essence of Laurocerasus and of Bitter Almonds. By M. Fileti (*Gazzetta chimica italiana*, **8**, 446—452).—The great difficulty of separating the whole of the hydrogen cyanide from essence of bitter almonds, and of the laurocerasus, renders it probable that it is present in some form of combination with the benzaldehyde; this compound would be the nitril,

$$C_6H_5.CH(OH).CN,$$

corresponding with mandelic acid. In order to test the truth of this supposition, the crude essences were treated with zinc and hydrochloric acid, in presence of alcohol and a platinum plate; 24 hours afterwards, the mixture was precipitated with water, and evaporated at 100° to remove alcohol. After filtration from the hydrobenzoïn, the liquid was supersaturated with potash, and agitated with ether, the ethereal solution being subsequently washed with water, and agitated with dilute hydrochloric acid. On evaporating the acid solution, the hydrochloride of a base was obtained, which was converted into the platinochloride and analysed, as was also the hydrochloride. The results correspond with the formula $C_6H_5.CH_2.CH_2.NH_2$ for the base. From this it would appear that the nitril $C_6H_5.CH(OH).CN$ is present in the crude essences, and that by the action of nascent hydrogen it is not converted into the amide $C_6H_5.CH(OH).CH_2.NH_2$, as might have been expected, but that an atom of oxygen is eliminated in the process, so that the final product is the base $C_6H_5CH_2.CH_2.NH_2$. A mixture of *pure* benzaldehyde and hydrogen cyanide, when treated with zinc and hydrochloric acid in a similar manner, yields a base having the composition and properties of methylamine.

In a similar manner, both chlorine and fuming sulphuric acid act differently on the essences to what they do on a mixture of pure benzaldehyde with hydrogen cyanide. With the crude essence, a solid crystalline substance is formed, which Zinin has shown to be benzylideneformobenzamide, Ph.CH(OH).CO.N : CHPh; whilst the author finds that no solid substance is produced by the action of fuming sulphuric acid on the mixture, and with chlorine it yields ammonium chloride and monochlorobenzoic chloride.

The base above described is obtained in much larger quantity by the action of zinc and hydrochloric acid on amygdalin in aqueous solution. The hydrochloride of the base is more soluble in water than in alcohol, crystallising from the latter in large plates, melting at 217°, and subliming near its fusing point. It would appear to be identical with that obtained by Colombo and Spica, by the action of nascent hydrogen on the compound of benzyl cyanide with hydrogen sulphide (*Gaz.*, **5**, 124). On decomposing the solution of the hydrochloride with potash, agitating with ether, and leaving the ethereal solution to evaporate, the free base is obtained as a syrupy liquid, which after a time crystallises in large plates (m. p. 101—104°). The author proposes to continue his examination of the more obscure reactions of the essences of bitter almonds and laurocerasus. C. E. G.

Aldehydes from Orcinol and their Derivatives. By F. Tiemann and E. Helkenberg (*Deut. Chem. Ges. Ber.*, **12**, 999—1005).

—When a solution of orcinol in very dilute soda is boiled with chloroform, three aldehydes are formed; they may be separated by acidifying the mixture with sulphuric acid and distilling in steam, when *α-orcindialdehyde* will be found in the distillate. By extracting the residue in the retort with ether, a mixture of *orcylaldehyde* and *β-orcendialdehyde* is obtained, from which the latter is removed by shaking up the ethereal extract with a solution of sodium hydrogen sulphite.

Orcylaldehyde, $C_6H_2Me(OH)_2.COH$.—The crude product is purified by solution in potash, and reprecipitation by acids; it is then recrystallised from benzene, and finally from water. The pure substance forms colourless needles (m. p. 177°), which dissolve freely in alcohol, ether, chloroform, hot benzene, and boiling water.

It unites with aniline to form orcylaldehydeanilide,

$$C_6H_2Me(OH)_2.C(NPh)H,$$

which crystallises in yellow prisms (m. p. 125°), soluble in alcohol, ether, and chloroform.

Homoacetoxycoumarin, $Me.(\bar{A}cO)C_6H_2<\overset{\text{—O—}}{CH:CH}>CO$, obtained by the action of acetic anhydride and sodium acetate on orcylaldehyde, crystallises in colourless needles (m. p. 126°), which are soluble in alcohol and ether. This compound gives a blue coloration with alkalis.

α-Orcendialdehyde, $C_6HMe(OH)_2(COH)_2$, forms long needle-shaped crystals (m. p. 117°), soluble in alcohol, ether, chloroform, and in hot water. This aldehyde unites with aniline, forming *α-orcendialdehydedianilide*, $C_6HMe(OH)_2[C(PhN)_2H]_2$, a yellow crystalline powder, which melts at 281°.

β-orcendialdehyde is obtained in pale yellow crystals by decomposing the sodium sulphite double compound with sulphuric acid, extracting with ether, and recrystallising from benzene and from dilute alcohol. This substance melts at 168°, but sublimes at a lower temperature. It is soluble in alcohol, ether, chloroform, benzene, and hot water.

W. C. W.

Derivatives of Tropic Acid. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **12**, 947—948).—*Tropide*, $C_9H_8O_2$, a syrupy liquid, is obtained by heating tropic acid to 160°, or by the action of strong hydrochloric acid on tropic acid at 180°. When heated at 60° with slaked lime, it yields calcium tropate.

Ethyl tropate, $C_9H_7EtO_3$, is an uncrystallisable syrup.

Chlorhydratropic acid, $C_9H_7ClO_2$, obtained by treating with water the product of the action of phosphorus pentachloride on tropic acid, crystallises in needles, which melt at 85°. W. C. W.

Umbelliferone Derivatives. By F. Tiemann and C. L. Reimer (*Deut. Chem. Ges. Ber.*, **12**, 993—999).—*Umbelliferone*, $C_9H_6O_3$, or $C_6H_3(OH)<\overset{\text{—O—}}{CH:CH}>CO$, is prepared by subjecting an alcoholic extract of galbanum resin to dry distillation, and extracting the distillate with hot water. It is deposited from the aqueous extract in colourless needles (m. p. 223°), which dissolve readily in alcohol. 100 parts of boiling water dissolve 1 part of umbelliferone. This sub-

stance dissolves in strong acids, but is reprecipitated on the addition of water. When a solution of umbelliferone in potash is heated to 60°, it takes up two atoms of hydrogen, forming umbellic acid.

Acetumbelliferone, $C_{11}H_8O_4$, or $C_9H_5O_3\bar{A}c$, prepared by the action of acetic chloride or anhydride on umbelliferone, melts at 140°, and dissolves freely in alcohol and ether. It is identical with the β-acetumbelliferone, or acetoxycoumarin of Lewy and Tiemann (*Ber.*, **10**, 2215; and this Journal, 1878; Abst., 424).

Methylumbelliferone, $C_9H_5(CH_3)O_3$, obtained by digesting a solution of umbelliferone in methyl alcohol with methyl iodide and potash, crystallises in glistening scales (m. p. 114°), which are soluble in alcohol and in ether. The crystals dissolve in sulphuric acid, forming a blue fluorescent solution, but are reprecipitated by the addition of water. Methylumbelliferone is not attacked by a boiling solution of potash.

The dioxybenzoic acid which is formed, together with resorcinol, when umbelliferone is fused with potash, splits up into carbonic anhydride and resorcinol at 200°. W. C. W.

A Homologue of Phosphenyl Chloride. By A. Michaelis (*Deut. Chem. Ges. Ber.*, **12**, 1009).—A liquid having the composition $C_7H_7PCl_2$ is formed by boiling a mixture of toluene, aluminium chloride, and phosphorus chloride. This substance, which boils at 240°, is either tolylphosphorus chloride, $C_6H_5.CH_2.PCl_2$, or benzylphosphorus chloride, $C_6H_4(Me).PCl_2$. It is decomposed by water, forming $C_7H_7PO_2H_2$. It unites with chlorine, yielding a solid tetrachloride, which is converted into the phosphinic acid, $C_7H_7PO_3H_2$, by the action of water. W. C. W.

Researches on Perchlorination. By H. H. Zetter, Ruoff, and Moë (*Deut. Chem. Ges. Ber.*, **12**, 677).—These experiments show that bodies containing a diphenyl complex in the molecule yield a perchlorodiphenyl. Diphenyl- and triphenyl-benzene do not split up on perchlorination. The formation of perchlorodiphenyl will in some cases throw light on the nature of a body; *e.g.*, ditolyl yields perchlorodiphenyl and perchloromethane, whilst the isomeric dibenzyl gives perchlorobenzene and perchlorethane.

Phenanthrene, which passes for an undoubted diphenyl compound, forms perchlorobenzene, instead of perchlorodiphenyl: hence the diphenyl nucleus of phenanthrene is formed by metamorphoses in its oxidation, and the formula of phenanthrene is of the type

$$C_6H_4 : CH.CH : C_6H_4,$$

and experiments in this direction would no doubt lead to its being obtained synthetically. The cyanogen group could not be eliminated by energetic chlorination of benzonitril and naphthonitril, as they give rise to chlorinated nitrils. Bromination of benzonitril yielded analogous results. Heating mercury cyanide with excess of bromine at 350° did not cause the cyanogen radicle to split up with formation of perbromomethane and elimination of nitrogen. G. T. A.

Nitration of Bromonaphthalene. By E. Labhardt (*Deut. Chem. Ges. Ber.*, **12**, 679).—When bromonaphthalene is added to cold

fuming nitric acid, two products are obtained. The less soluble one can be easily isolated; it melts at 169·5°. It crystallises from alcohol in white needles, and consists of dinitrobromonaphthalene. A warm mixture of nitric and sulphuric acids converts it into trinitrobromonaphthalene, which crystallises easily, melts at 184·5°, and appears to be completely converted into trinitronaphthol when treated with alkalis. G. T. A.

Oxidation of Nitronaphthalene. By Beilstein and Kurbatoff (*Deut. Chem. Ges. Ber.*, **12**, 688).—Chromic acid oxidises a solution of nitronaphthalene in acetic acid to nitrophthalic acid (m. p. 212°) and its aldehyde (m. p. 135°). Nitrophthalic acid is decomposed by hydrobromic acid, with formation of carbonic anhydride, and di- and tri-bromobenzoic acids, whilst hydriodic acid converts it into metamidobenzoic acid. G. T. A.

Halogen-derivatives of β-Naphthol. By A. J. Smith (*Deut. Chem. Ges. Ber.*, **12**, 680).—The monobromo-compound, $C_{10}H_6Br.OH$, is easily prepared by dropping the calculated weight of bromine into cold solution of β-naphthol in acetic acid. It melts at 84°, and crystallises from dilute acetic acid in long slender needles. When strongly heated it evolves hydrobromic acid, and leaves an easily crystallisable body. It also yields a crystalline body when fused with potash.

G. T. A.

Dichloronaphthalene-β-sulphonic Acid. By O. Widmann (*Deut. Chem. Ges. Ber.*, **12**, 963—967).—This acid, $C_{10}H_5Cl_2.SO_3H$, which is obtained by the action of water at 130° on dichloronaphthalene-β-sulphonic chloride (m. p. 133°), is a white powder, soluble in warm water. It forms the following salts:—$C_{10}H_5Cl_2.SO_3K + 5H_2O$, deposited from a warm solution in slender needles; $2(C_{10}H_5Cl_2.SO_3K) + 5H_2O$ separates out in white prisms from a hot concentrated solution.

$$2C_{10}H_5Cl_2.SO_3K + 3H_2O$$

remains when the solution is evaporated on a water-bath. When these salts are dried in a desiccator they lose $4\frac{1}{2}$, 4, and 2 mols. of water respectively. The ammonium salt may be obtained in slender needles or in transparent plates. $C_{10}H_5Cl_2.SO_3Ag + H_2O$ is a white crystalline powder, sparingly soluble in cold water. $(C_{10}H_5Cl_2.SO_3)_2Ba + 4H_2O$, $(C_{10}H_5Cl_2.SO_3)_2Ca + 2H_2O$, and $(C_{10}H_5Cl_2.SO_3)_2Pb + 4H_2O$, crystallise in white needles, which are but slightly soluble in cold water. $(C_{10}H_5Cl_2.SO_3)_2Mn + 7H_2O$, white glistening plates, sparingly soluble in warm water. $(C_{10}H_5Cl_2.SO_3)_2Zn + 13H_2O$, microscopic needles, freely soluble in warm water.

The copper salt forms pale blue needles, which are more soluble in water than most of the preceding salts.

The *amide*, $C_{10}H_5Cl_2.SO_2NH_2$, prepared by the action of ammonia on the corresponding chloride, is deposited from an alcoholic solution in silky needles, which melt and blacken at 245°. W. C. W.

Action of Chlorine on Naphthalene-β-sulphonic Chloride: a New Trichloronaphthalene. By O. Widmann (*Deut. Chem. Ges.*

Ber., **12**, 959—963).—The *tetrachloride* of *naphthalene-β-sulphonic chloride*, $C_{10}H_7.SO_2Cl.Cl_4$, is formed when chlorine (2 mols.) is passed through a solution of naphthalene-β-sulphonic chloride (1 mol.) in chloroform or carbon bisulphide, and it is deposited in lustrous cubes (m. p. 131°), when the liquid is allowed to evaporate at the temperature of the air. The crystals dissolve in chloroform, carbon bisulphide, and in boiling acetic acid.

If the oily mother-liquor from the tetrachloride is boiled with alcoholic potash, and the potassium salt treated with phosphorus pentachloride, *dichloronaphthalene-β-sulphonic chloride*, $C_{10}H_5Cl_2.SO_2Cl$, is obtained in needle-shaped crystals (m. p. 133°), which are soluble in benzene and carbon bisulphide. When this substance is heated in sealed tubes with water, dichloronaphthalene-β-sulphonic acid is formed.

ζ-Trichloronaphthalene, $C_{10}H_5Cl_3$, prepared by distilling dichloronaphthalene-β-sulphonic chloride with phosphorus pentachloride, crystallises in white needles (m. p. 56°), soluble in benzene. It yields nitrodichlorophthalic acid, when treated with nitric acid, sp. gr. 1·2, in sealed tubes at 150°.

Six trichloronaphthalenes are now known, viz.:—

α	m. p. 81°	δ	m. p. 131°
β	„ 90	ε	„ 65
γ	„ 103	ζ	„ 56

The author considers that the tetrachloride of naphthalene-β-sulphonic chloride has the constitution

$$SO_2Cl:Cl:Cl:Cl = [3:1'2:3':4'].$$ W. C. W.

Naphthylcarbamides. By S. Pagliani (*Gazzetta chimica italiana*, **9**, 28—32).—Naphthylamine, purified by Papasogli's method of converting it into the bisulphite, and exposing the crystals over lime, was heated at 120° for some hours with rather less than half its weight of urea, both carefully dried. Ammonia is evolved during the reaction, and when cold, the product after being treated with boiling water, is crystallised from alcohol. The *dinaphthylcarbamide*, $CO(NH.C_{10}H_7)_2$, thus obtained forms silky needles insoluble in water, and only very sparingly soluble in boiling alcohol. It melts at 270° with decomposition, and is identical with the compound obtained by Delbos, and subsequently by Zinin, on distilling hydrogen-naphthylamine oxalate.

On heating naphthylamine hydrochloride with urea at 150—170°, and boiling the product with very dilute hydrochloric acid, the aqueous solution deposits crystals on cooling, which have all the properties of Schiff's *mononaphthylcarbamide*, $CO(NH.C_{10}H_7).NH_2$ (*Chem. Centr.*, 1857, 166). It is only sparingly soluble in water or ether, but dissolves easily in alcohol. The portion of the crude product insoluble in boiling water was found to be dinaphthylcarbamide.

These results show that when the free base acts on urea, nothing but the bi-substituted derivative of carbamide is formed, which is in accordance with the investigations of Baeyer, Genz, and Girard, in the same direction. With the hydrochloride of the base, however, both the mono- and the bi-substituted derivatives are formed.

The formula $CO(NH.C_{10}H_7)_2$, ascribed to the dinaphthylcarbamide, represents a hydrogen-atom of each NH_2-group of carbamide as displaced by naphthyl, $C_{10}H_7$: for when it is decomposed by boiling with potash it yields naphthylamine, but no ammonia: moreover, it is identical in its properties with Delbos and Zinin's dinaphthylcarbamide, obtained by heating naphthylamine-hydrogen oxalate. In this case, as Zinin showed, the oxalate is converted into naphthylformamide and then into the naphthyloxamide, which is decomposed in the following manner:—

$$C_{10}H_7.NH.CO.CO.NH.C_{10}H_7 = C_{10}H_7.NH.CO.NH.C_{10}H_7 + CO.$$

C. E. G.

α-Diamidanthraquinone. By v. Perger (*J. pr. Chem.* [2], **19**, 209—222).—Alizarin is produced by fusing α-diamidanthraquinone with potash. The simplest explanation of this reaction is to regard it as a substitution of OH for NH_2, thus, $C_{14}H_6O_2(NH_2)_2 + 2H_2O = C_{14}H_6O_2(OH)_2 + 2NH_3$.

But the author's previous researches (this Journal, p. 253) have shown that alizarin and α-diamidanthraquinone belong probably to different series of di-substitution derivatives; and that in the production of alizarin from mono-substitution derivatives by fusion with potash, one OH group replaces the substituting radicle, whilst the other enters the molecule by "direct exchange" for hydrogen. It is therefore probable that in the production of alizarin from α-diamidanthraquinone, a change occurs in the position of the replacing groups, and that the two OH groups in the former compound do not occupy the same positions as the two NH_2 groups in the latter.

In order to test the accuracy of this hypothesis, the author prepared α-diamidanthraquinone-monosulphonic acid by acting on the α-diamido-compound with fuming sulphuric acid, and converted this into anthraquinone-monosulphonic acid by the action of nitrous acid. This acid he found to be identical with the anthraquinone-monosulphonic acid prepared directly from anthraquinone itself. Hence he concludes that one of the NH_2 groups in α-diamidanthraquinone must have a position different from either of the hydroxyl groups in alizarin, and that in fusing α-diamidanthraquinone with potash a change of position occurs among the replacing groups.

Anthraquinone-monosulphonic acid when fused with potash yields monhydroxyanthraquinone, and as the same mono-sulphonic acid is obtained from anthraquinone as from α-diamidanthraquinone, it would appear that neither of the NH_2 groups in the α-diamido-compound can occupy the same position as the OH group in monohydroxyanthraquinone.

But alizarin is produced from α-diamidanthraquinone, and as it has been shown that but one hydrogen atom is directly replaced by hydroxyl on fusion with potash, it follows that change of position can occur in one of the NH_2 groups only, and that one of these groups must occupy the same position as one of the OH groups in alizarin. Böttger and Petersen (*Annalen*, **160**, 148) obtained alizarin by fusion of that mononitranthraquinone, the diazo-compound of which, when treated with water, yielded monhydroxyanthraquinone. From the

same mononitranthraquinone, α-diamidanthraquinone was also obtained. From these reactions it follows that the NO_2 group in the mononitro-compound occupies the same position as the OH group in monhydroxyanthraquinone, and that one NH_2 group in the α-diamido-compound also occupies this position.

The contradiction involved in these two conclusions is only apparent. The following formulæ (see this Journal, p. 256) show the connection which the author believes to exist among the various compounds, and represent the SO_3H group of α-diamidanthraquinone monosulphonic acid, and one of the NH_2 groups of α-diamidanthraquinone as occupying the same position as the OH-group of monohydroxyanthraquinone.

$C_6H_4(CO)_2C_6H_3(OH)_{II}$.
Monhydroxyanthraquinone.

$C_6H_4(CO)_2C_6H_3(NO_2)_{II}$.
Mononitroanthraquinone.

$(NO_2)C_6H_3(CO)_2C_6H_3(NO_2)_{II}$.
α-Dinitroanthraquinone.

$(NH_2)C_6H_3(CO)_2C_6H_3(NH_2)_{II}$.
α-Diamidanthraquinone.

$$\begin{matrix}NH_2\\(SO_3H)_{II}\end{matrix}C_6H_2(CO)_2C_6H_3(NH_2)_{II}.$$
α-Diamidanthraquinone-monosulphonic acid.

$(SO_3H)_{II}C_6H_3(CO)_2C_6H_4$.
Anthraquinone-monosulphonic acid.

$(OH)_{II}C_6H_3(CO)_2C_6H_4$.
Monhydroxyanthraquinone.

For details of preparation and properties of the various compounds mentioned, reference must be made to the original: an improved method for preparing α-diamidanthraquinone is described.

M. M. P. M.

Nitroalizarin. By E. Schunck and H. Römer (*Deut. Chem. Ges. Ber.*, **12**, 1008).—The authors point out, that in their previous communication on nitroalizarin (*Ber.*, **12**, 584) they omitted to state that Caro was the first to use a mixture of nitric acid with glacial acetic acid or nitrobenzene for nitrating alizarin. W. C. W.

Essence of Rosemary. By Bruylants (*J. Pharm.* [4], **29**, 508—511).—The quantity of essential oil yielded by the plant *Rosmarinus officinalis* depends on the latitude in which it is grown; that from the neighbourhood of Paris yielding only 1·4 to 1·6 grams per kilo., whilst that grown in the south of France yields 3 grams per kilo. When freshly prepared, it is a colourless liquid, but on keeping it darkens in colour and becomes thick; it is miscible in all proportions with alcohol of 85 per cent. It smells strongly of rosemary, its taste is hot and camphorous; its sp. gr. at 12° is 0·885; it turns the plane of polarisation to the left. It begins to boil at 150°, and the temperature gradually rises to 200°, where it remains stationary a short time, and finally rises to 260°. By fractional distillation, it may be separated into three portions, boiling from 150° to 180°, from 180° to 210°, and from 210° to 260°.

Fraction boiling between 150° *and* 180°.—By repeated distillation and rectification over sodium, a liquid is obtained boiling at 157—160°,

which is lævogyrate. Its vapour-density corresponds with the formula for terpene, $C_{10}H_{16}$. This terpene combines with iodine, and on distilling the product, it decomposes into hydriodic acid and cymene, $C_{10}H_{14}$; by the action of nitric acid, it yields γ-toluic acid.

Fraction boiling between 180° *and* 210°.—By careful distillation, a liquid boiling at 200—205° is obtained, which on cooling deposits crystals melting at 176°, and boiling at 204°. They possess all the properties of laurel camphor. The mother-liquor boils at a lower temperature, and on distillation yields a second crop of crystals and some terebene. Repeated distillation results in the complete separation of these two bodies.

Fraction boiling between 210° *and* 260°.—By cooling this fraction in a freezing mixture, a large quantity of borneol is separated, which when treated with phosphoric anhydride, yields a hydrocarbon of boiling point 160°, and having the vapour density 5·23 (Air = 1). This, when treated with iodine, yields cymene and hydriodic acid. Amongst the products of the action of nitric acid are borneol, and a crystalline body which melts at the same temperature as camphor.

When distilled with acetic anhydride, the borneol yields a product boiling at 230°, which is decomposed by potash, with formation of a hydrocarbon, $C_{10}H_{16}$, and potassium acetate.

Essence of rosemary therefore contains—

A hydrocarbon (lævogyrate), $C_{10}H_{16}$	80 per cent.
A borneol camphor, $C_{10}H_{18}O$	4 to 5 „
A camphor, $C_{10}H_{16}O$.....	6 to 8 „

When acted on by concentrated sulphuric acid, essence of rosemary yields a mixture of cymene (b. p. 175°), and terpene (b. p. 16°), and on oxidation with chromic mixture, it yields a small quantity of camphor, some formic and acetic acids, and terephthalic acid.

The author gives no analyses. L. T. O'S.

Hydration of Terpenes. By F. Flawitzky (*Deut. Chem. Ges. Ber.*, **12**, 1022).—The lævogyrate terpene from French oil of turpentine and the dextrogyrate terpene from Russian turpentine, both form hydrates on adding water to a mixture of the terpene with alcohol and sulphuric, nitric, or hydrochloric acid, which has been left at rest for 10 days.

On warming four parts of the lævogyrate terpene with one part of alcohol and one part of sulphuric acid, sp. gr. 1·64, a liquid is formed which boils at 175°, and has no action on polarised light.

W. C. W.

Transformation of Camphic Acid into Camphor. By J. de Montgolfier (*Compt. rend.*, **88**, 915).—The author has succeeded in converting camphic acid into camphor by Piria's method of heating a mixture of the calcium salt with calcium formate, $(C_{10}H_{16}O_2)_2Ca + (H.COO)_2Ca = 2C_{10}H_{16}O + 2CaCO_3$. The camphor remains dissolved in the most abundant product of the reaction, a liquid (b. p. 230—235°) of the composition of phorone, but which the author believes to be isomeric and not identical with it. R. R.

The Glucoside of Liquorice. By F. Sestini (*Gazzetta chimica italiana*, 8, 454—462).—An aqueous extract of the root, on being evaporated to dryness after treatment with animal charcoal, yields a product from which absolute alcohol extracts asparagine. The residue dissolves in dilute spirit, and when burnt leaves an ash containing lime, alkalis, and a trace of sulphuric acid. From these results, it is evident that glycyrrhizin does not exist in the root in the free state, but in combination with bases, chiefly lime. An examination of the commercial extract, or "liquorice," shows that it contains free glycyrrhizin in small quantity, liberated, apparently, from its combinations by the acids formed during the evaporation of the juice. Roussin (*Jour. Pharm.*, 1875) imagined that the glycyrrhizin existed in the root as an ammonium compound containing 0·14 per cent. nitrogen; but, as the author points out, the method by which he obtained this compound (precipitating the glucoside with sulphuric acid, and treating it first with alcohol and ether, and then with an alcoholic solution of ammonia), affords no evidence that it existed in the root as such, and moreover it is not very probable that the substance obtained by Roussin is a definite compound, as it would contain 26 or 27 molecules of glycyrrhizin to one of ammonia.

The glucoside dissolves in dilute potash solution, and is precipitated again unaltered by acids, but the potassium compound formed could not be isolated. Better success attended the attempts to prepare the calcium and barium compounds. *Calcium glycyrrhizate*, prepared by adding calcium chloride to a solution of the glucoside in the smallest excess of potash, washing the precipitate with water, and drying at 100°, forms a brown shining mass. By dissolving glycyrrhizin in milk of lime, filtering, separating the excess of lime by carbonic acid, and evaporating, a residue is obtained, which when treated with alcohol of 50 per cent. and evaporated, yields the glycyrrhizate in amorphous yellowish scales. This glycyrrhizate is hygroscopic, and has a sweet taste: it is almost insoluble in dry alcohol, but dissolves tolerably well in dilute alcohol.

It is only sparingly soluble in water, but more readily in presence of calcium hydrate, which points to the existence of a basic compound.

Dried at 110° and analysed, it gave numbers corresponding with the formula $3CaO + 5C_{24}H_{36}O_9$, adopting Gorup-Besanez' formula, $C_{24}H_{36}O_9$, for glycyrrhizin.

Barium glycyrrhizate, $3BaO + 5C_{24}H_{36}O_9$, obtained in a manner similar to the calcium compound by dissolving glycyrrhizin in baryta-water, passing carbonic anhydride, and evaporating, forms yellowish scales. All the compounds of glycyrrhizin with bases have a sweet taste; glycyrrhizin itself when first placed on the tongue is insipid, but as it dissolves in the alkaline saliva, it acquires a sweet taste.

The ordinary method of preparing glycyrrhizin by exhausting the root with water and precipitating with sulphuric acid, gives very unsatisfactory results, as the product is small and highly coloured, and there is great difficulty in separating the adherent sulphuric acid. The author prefers to exhaust the root four or five times successively with boiling water and a little milk of lime, and to precipitate the

concentrated extract with acetic acid. The brownish gelatinous precipitate, after being washed with water, is dissolved in spirit of 50 per cent., decolorised by animal charcoal, and evaporated on the water-bath until the alcohol is expelled. On cooling, it solidifies to a gelatinous mass, which is dissolved in alcohol, mixed with twice its volume of ether, filtered and evaporated. The gelatinous glycyrrhizin is then pressed and dried over sulphuric acid. The author regards the crystalline substance obtained by Habermann (*Wien Akad. Ber.*, **74**, ii) as an alteration product.

In order to determine the amount of glycyrrhizin in the root, it is extracted eight times successively with boiling water rendered alkaline by calcium hydrate, and the solution concentrated to a syrup is precipitated with 10 per cent. acetic acid, which has been previously saturated with glycyrrhizin, as is also the dilute acid (2 per cent.), and water used for washing. The precipitated glycyrrhizin is then dissolved in alcohol, and the solution evaporated after treatment with animal charcoal. In this way the fresh root containing 48 per cent. water yields 3·271 per cent. glycyrrhizin, or 6·318 on the dry root.

C. E. G.

Preliminary Notice on Teucrium Fruticans. By A. Oglialoro (*Gazzetta chimica italiana*, **8**, 440—446).—This labiate plant, which is employed as a febrifuge, is called "olivetta" by the Italian peasants, from the resemblance of its leaves in colour to those of the wild olive. The fresh plant collected in June soon after flowering gave no essential oil when distilled with water; it was therefore dried in the sunshine, and treated with boiling alcohol in a continuous displacement apparatus for two days. On cooling, the extract deposited a deep green granular pasty substance. The partly exhausted plant was then treated for other two days with fresh spirit, and on cooling, a nearly colourless crystalline substance was deposited from the solution.

The green deposit from the first extract consists of two substances mixed with a large quantity of chlorophyll. When treated with boiling alcohol, a white crystalline substance is left undissolved, identical with the crystalline deposit from the second extract. The other compound, which is readily soluble in hot alcohol and in benzene, can only be freed from chlorophyll with difficulty. It is a nearly white somewhat soft substance, insoluble in water, and melting at about 80—85°. As it does not crystallise, and constant analytical results could not be obtained, the author is inclined to consider it as a mixture.

Teucrin.—The nearly colourless crystalline substance obtained from *T. fruticans* dissolves but very sparingly in any of the ordinary solvents, with the exception of glacial acetic acid, which affords the best means of purifying it. It crystallises in slender prisms of a yellowish colour, which melt at 228—230° with decomposition. The results of the analyses accord best with the formula $C_{21}H_{24}O_{11}$, but the author reserves his opinion on this subject until he has more thoroughly investigated the nature of the substance. Teucrin is decomposed when heated with dilute nitric acid, leaving a residue of a red colour; on cooling, the solution deposits yellow crystals, which may be purified by recrystallisation from boiling water. The new substance is thus

obtained in long silky prisms (m.p. 180°) of a golden colour. It is of an acid nature, and yields a silver salt, rather soluble in water, but which is thrown down in splendid golden-yellow plates on adding alcohol or ether to a mixture of the ammonium salt with silver nitrate. The analysis of the acid itself and that of the silver salt points to the formula $C_8H_8O_3$ for the acid, which is that of hydroxytoluic acid; its fusion point also is nearly the same as that of Fittica's β-hydroxytoluic acid (*Ber.*, **7**, 927). The nitric acid mother-liquors, from which this acid crystallises, contain oxalic and tartaric acids, indicating that the substance is a glucoside. Teucrin is decomposed when boiled with dilute sulphuric acid, leaving a yellow residue of an acid nature, the quantity of which was too small to establish its identity with the acid obtained by the action of nitric acid; the solution contains a substance of the nature of glucose, so that there can be no doubt that teucrin is a glucoside. Three 0·5 gram doses of teucrin administered to a dog caused a lowering of the temperature of the animal. C. E. G.

Picrotoxin. By E. Paternò and A. Oglialoro (*Gazzetta chimica italiana*, **9**, 57—64).—In former papers (this Journal, 1877, i, 719, and ii, 790) the authors described picrotoxide, $C_{15}H_{16}O_6$, and hydrate of picrotoxide, $C_{15}H_{18}O_7$, obtained by the action of hydrochloric acid on picrotoxin suspended in ether, and also a substance, $C_{15}H_{15}BrO_6$, regarded as monobromopicrotoxide, formed by the action of bromine on the hydrate of picrotoxide. This hydrate can be easily prepared by saturating a boiling alcoholic solution of picrotoxin with dry hydrochloric acid, and distilling off the alcohol; the residue is then dissolved in water and agitated with ether, which on evaporation leaves the hydrate of picrotoxide in the crystalline state. It may be purified by recrystallisation from boiling water. In their last paper (*loc. cit.*, p. 790) the authors stated that by the action of acetic chloride on the hydrate of picrotoxide they had obtained a crystalline compound, which they believed to be a diacetyl derivative, $C_{15}H_{16}O_7\bar{A}c_2$. As, however, the results of the elementary analysis cannot afford any definite evidence as to whether it was a monacetyl or diacetyl derivative, the percentage of carbon in the two formulæ differing by 0·09 only—the benzoyl derivative was prepared by the action of benzoic chloride on the hydrate of picrotoxide. It crystallises in colourless prisms (m. p. about 230°), which on analysis were found to have the composition indicated by the formula $C_{15}H_{17}O_7\bar{B}z$. It is almost certain therefore that the acetyl-compound has a similar composition, $C_{15}H_{17}O_7\bar{A}c$.

By the action of acetic anhydride and sodium acetate on picrotoxin, two crystalline substances are produced, one of which (m. p. 227°) is formed only in very small quantity; the other, after being purified by crystallisation from boiling alcohol, is obtained in large colourless prisms (m. p. 245°), sparingly soluble in ether, but easily in chloroform. When boiled with potash, or even when heated with water at 150°, it is decomposed with elimination of acetic acid; this circumstance and the analytical results show that it is an acetyl-compound of the formula $C_{19}H_{20}O_8$. By the action of bromine a compound is produced, crystallising in prisms (m. p. 180°), which are soluble in alcohol, ether,

and chloroform; but whether this is a dibromo-derivative, $C_{19}H_{18}Br_2O_8$, or an addition product, $C_{19}H_{20}O_8Br_2$, could not be ascertained by analysis. As, however, but little hydrobromic acid was evolved during the reaction, and the melting point of the derivative is lower than that of the parent compound, it is probably an addition product. The results obtained by the action of hydrobromic acid were unsatisfactory; a crystalline substance containing bromine is formed, which melts at about 150°, but the analytical numbers did not correspond with the formula $C_{19}H_{20}O_8.HBr$.

With regard to the chief product of the action of acetic anhydride and sodium acetate on picrotoxin, the authors are inclined to believe that it is an unsaturated compound, but a derivative of picrotoxide.

C. E. G.

Supposed Identity of Columbin and Limonin. By E. Paternò and A. Oglialoro (*Gazzetta chimica italiana*, **9**, 64—67).—Schmidt (*Annalen*, **41**, 338) considered that limonin was identical with the colombin extracted from colombo root by Wittstock (*ibid.*, **19**, 298); and as the authors found much difficulty in preparing limonin in quantity from the seeds of the lemon and orange, whilst colombin could be obtained with comparative ease, they determined to examine into the question of the supposed identity of the two substances. The yield of limonin is but small, only 80 grams of the impure substance having been obtained from 15,000 grams of the seeds. It crystallises in beautiful lustrous plates, and has the characters ascribed to it by Schmidt, except that it melts at 275° and not at 244°: moreover, it not only dissolves in potash without alteration, but also in baryta-water, forming a kind of salt, which is not decomposed by carbonic anhydride. The formula which agrees best with the analytical results is $C_{26}H_{30}O_8$; this requires C = 66·38; H = 6·38.

When colombo root is extracted with ether and the solution is evaporated, a crystalline residue is obtained which, after being washed with a little cold ether to remove fatty matters, &c., is treated with boiling alcohol: on cooling, the solution deposits colourless prismatic crystals, which melt at 182°, and have all the properties of Wittstock's colombin. The results of the elementary analysis agree with the formula $C_{21}H_{22}O_7$, which requires C = 65·28; H = 5·69.

When the residue which is left after the separation of the colombin, and is almost insoluble in alcohol, is crystallised from boiling glacial acetic acid, it yields a second substance, having a melting point of 218—220°. Both this compound and Wittstock's columbin are therefore quite distinct from limonin.

C. E. G.

Colouring Matter of the Caryophyllaceæ. By A. Hilger and H. Bischoff (*Landw. Versuchs.-Stat.*, **23**, 456—461).—*Phytolacca decandra.*—The alcoholic solution of the colouring matter of the ripe berries gives an absorption spectrum with two characteristic bands in the green; under the action of alkalis the absorption becomes continuous. Similar effects are obtained with the alcoholic solution of the colouring matter of *Beta vulgaris* (*rubra*), *Chenopodium quinoa*, *Amaranthus salicifolius* (*caudatus*), and *portuloca*. The juice of the fruit of the latter, diluted with an equal volume of alcohol, is de-

colorised on addition of potash, the colour is restored by acids only when added within a short interval. In this respect, as in the other optical characteristics of their solutions, the authors regard the red colouring matters of the several orders of the Caryophyllaceæ as identical. The chemical investigation of the colouring matter of *phytolacca* is in progress. C. F. C.

Oxidation of Quinoline. By S. Hoogewerff and Van Dorp (*Deut. Chem. Ges. Ber.*, **12**, 747—748).—Quinoline, when oxidised by boiling with solution of potassium permanganate, yields a pyridenedicarbonic acid, $C_7H_5.NO_4$. It crystallises in short shining prisms, which when heated blacken and melt at 222—225°; this is the melting point of pyridene-carbonic acid (Laiblin, *Ber.*, **10**, 2136), into which it is possible this acid may be decomposed by heat. Pyridinedicarbonic acid is sparingly soluble in cold, more easily in hot alcohol and water, and insoluble in ether and benzene.

The *barium* salt, $C_7H_3NO_4Ba$, and *silver* salt, $C_7H_3NO_4Ag_2$, are both gelatinous precipitates, becoming crystalline after heating in a water-bath for some time. By heating the calcium salts, alkaline distillates are obtained, having the odour of Dippel's oil. This acid is not identical with any of the pyridenedicarbonic acids described by Ramsay (this Journal, **196**, 262). The acid, $C_9H_9NO_3$, which Dewar obtained (*Jahresb.*, 1877, 445) by oxidation of quinoline with potassium permanganate, is a primary product, owing its formation to the proportion of oxidising agent used. In these experiments the authors used coal-tar quinoline, but intend to investigate the products of the oxidation of quinoline from cinchonine. P. P. B.

Oxidation of Cinchonine Quinoline by Potassium Permanganate. By W. Koenigs (*Deut. Chem. Ges. Ber.*, **12**, 983—984).—*Dicarbopyridenic acid* is formed by the action of a solution of potassium permanganate on quinoline. The acid is sparingly soluble in cold water, and the aqueous solution gives with ferrous sulphate a reddish-yellow coloration, with copper acetate a pale blue precipitate, and with silver nitrate a gelatinous precipitate soluble in hot water.

When the acid is heated, it melts, with evolution of carbonic anhydride, and a new acid sublimes. W. C. W.

Nicotine. By G. Andreoni (*Gazzetta chimica italiana*, **9**, 169—173).—Considering that nicotine yields pyridine so readily, that it forms addition compounds with bromine and iodine, and that many of the vegetable alkaloïds contain the methyl group and have the characters of tertiary amides, it seemed not improbable that nicotine might be a methylamine of the formula $NMe_2.C_3H_4-C\begin{matrix}CH-CH\\ \diagup\quad\quad\diagdown\\ CH=CH\end{matrix}\diagdown N$. The author therefore prepared some pure nicotine by Schloessing's process (*Ann. Chim. Phys.*, **19**, 231), and treated it both with hydrochloric and hydriodic acid at various temperatures and under various conditions, in hopes of eliminating methyl, and obtaining a nornicotine of the formula $NH_2\,C_3H_4.C_5H_4N$. The results, however, were negative, as no trace of methyl iodide or chloride could be detected in the product.

A portion of the nicotine, however, undergoes change, and traces of pyridine are produced together with a brownish substance, which is possibly a polymeride of nicotine. C. E. G.

A new Nicotine Derivative. By A. Cahours and A. Etard (*Compt. rend.*, 88, 999—1003).—Having the means of obtaining large quantities of nicotine, the authors have undertaken a series of experiments to determine its constitution. On oxidation nicotine gives carboxypyridenic acid, $C_6H_5NO_2$, which when heated in presence of alkalis splits up into carbonic anhydride and pyridine. Hence nicotine may be regarded as dipyridine, $C_{10}H_{10}N_2 + 4$ atoms of hydrogen. Inversely, by withdrawing H_4 from the molecule of nicotine, it might be possible to obtain dipyridine. Attempts to effect this by the action of the halogens have hitherto proved unsuccessful.

The action of sulphur on this alkaloïd might be expected to give rise to the formation of a substitution-product analogous to thianiline, the formation of an addition-product, or the production of dipyridine, which would afterwards be acted on by the sulphur. On heating 100 parts of nicotine with 20 parts of sulphur at 140°, sulphuretted hydrogen was given off, and continued to be evolved as the temperature rose to 155°. The perfectly fluid mass assumed a chrome-green colour at 160—170°, which temperature was not exceeded. On allowing it to stand for some days, yellow prismatic crystals separated in abundance. These, after being purified by washing with cold alcohol, and then recrystallised from boiling alcohol, have the composition $C_{20}H_{18}N_4S$. They are of a sulphur-yellow colour, slightly soluble in cold, but readily in hot alcohol, insoluble in water, slightly soluble in benzene, and still less so in ether. The crystals fuse at 155°, and on cooling form a resinous yellow mass. The substance has a perfectly neutral reaction, and when subjected to dry distillation evolves sulphuretted hydrogen, whilst carbon is deposited, and a small quantity of a volatile oil distils over.

The hydrochloride has the composition $C_{20}H_{18}N_4S.2HCl$, and crystallises in fine golden-yellow needles. The sulphate has not yet been obtained in a definite crystalline form. In solutions of the hydrochloride, platinum tetrachloride gives an amorphous yellow precipitate of $C_{20}H_{18}N_4S.2HCl.PtCl_4$. Mercuric chloride gives a chloromercurate, $C_{20}H_{18}N_4S.HCl.HgCl_2$, soluble in hydrochloric acid, and crystallising in yellow needles. Picric acid gives a salt soluble in water, and crystallising in yellow needles. Gold chloride gives an amorphous precipitate, soluble in hot water, from which it separates in brilliant scales. Potassium dichromate, ferro- and ferri-cyanide, iodide, and cyanide, all give yellow precipitates.

The authors consider that the nicotine is first transformed into *tetrapyridine*, $C_{20}H_{20}N_4$, by removal of hydrogen; $2(C_{10}H_{14}N_2) + 2S_2 = 4H_2S + C_{20}H_{20}N_4$, and that a substitution of sulphur for hydrogen then takes place: $C_{20}H_{20}N_4 + S_2 = H_2S + C_{20}H_{18}N_4S$. The substance is therefore *thiotetrapyridine*. Its relation to nicotine may be shown by the formula $(C_{10}H_9N_2)_2S$.

The action of an excess of sulphur at a higher temperature gives rise to another body not yet isolated. C. H. B.

Tropidine. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **12**, 944—947).—Tropidine, $C_8H_{13}N$, is prepared by the action of strong hydrochloric acid at 180° on a mixture of tropine or atropine and glacial acetic acid. The crude product is saturated with potash and extracted with ether. On evaporating the ethereal solution, the base remains as an oily liquid, boiling at 162°, and having the sp. gr. 0·9665 at 0°. The oil dissolves in a small quantity of water, but the solution becomes turbid when a large excess of water is added. The base forms crystalline double salts with the chlorides of gold and platinum, viz.: $(C_8H_{13}N.HCl)_2PtCl_4$ and $C_8H_{13}N.HClAuCl_3$.

The author points out the relation between collidine, $C_8H_{11}N$, tropidine, $C_8H_{13}N$, and coniine $C_8H_{15}N$. W. C. W.

Artificial Atropine. By A. Ladenburg (*Deut. Chem. Ges. Ber.*, **12**, 941—944).—Kraut and Lossen (*Annalen*, 138) have shown that atropine is decomposed by the action of baryta-water or hydrochloric acid into tropine and tropic acid, $C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3$.

By the action of dilute hydrochloric acid, at a temperature below 100°, on tropine tropate, atropine is formed, the artificial product being identical in its properties with the natural alkaloïd.

W. C. W.

Piperidine and Pyridine. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, **12**, 984—990).—*Piperidine*, $C_5H_{11}N$, is not decomposed by fuming hydrochloric acid at 300°. The hydrochloride combines directly with bromine to form a crystalline addition product, which rapidly decomposes even at the ordinary temperature. On heating this bromine compound, or a mixture of bromine and piperidine hydrochloride in sealed tubes at 200°, hydrobromic acid and a small quantity of bromoform are produced, and on the addition of water to the contents of the tubes, a substance having the composition $C_5H_3Br_2NO$ separates out in crystalline plates. The crystals are almost insoluble in cold water and ether; they dissolve in ammonia or soda solution, but are reprecipitated by dilute acids. They are decomposed by heat without melting. When platinic chloride is added to a solution of this substance in strong hydrochloric acid, the platinum double salt—

$$2(C_5H_3Br_2NO.HCl)PtCl_4,$$

is deposited in long needles, which are decomposed by water.

The *silver* salt, $C_5H_2AgBr_2NO$, is a sparingly soluble crystalline powder, and the *methyl* salt, $C_5H_2(CH_3)Br_2NO$, crystallises in white needles, which melt at 192°.

The existence of the above compounds seems to indicate the presence of a hydroxyl group in the piperidine derivative, *e.g.*,

$$C_5H_2Br_2(OH)N\,;\ C_5H_2Br_2(OAg)N.$$

Pyridine.—When bromine is added to a solution of pyridine hydrochloride, a crystalline orange-coloured substance is precipitated. On heating this precipitate, or a mixture of bromine and pyridine hydrochloride at 200°, *dibromopyridine*, $C_5H_3Br_2N$, separates out in needle-

shaped crystals, soluble in ether and in strong hydrochloric acid. It is precipitated from the acid solution by water. Dibromopyridine melts at 109°, but begins to sublime at 100°. It forms a double salt with platinic chloride, which crystallises in large rhombic plates. Baryta-water, ammonia, alcoholic potash, nitric acid, sulphuric acid, and potassium permanganate have no action on dibromopyridine.

Monobromopyridine (b. p. 170°) appears to be formed at the same time as the dibromopyridine. W. C. W.

Poisonous and Crystallisable Alkaloïd from an Exhumed Corpse containing Arsenic. By F. Selmi (*Gazzetta chimica italiana*, **9**, 33—34).—This substance was found in two bodies which had been buried 20 days and a month respectively, and in which on examination arsenic acid was detected in abundance. The viscera were exhausted with alcohol, the solution was concentrated at 35—40° in a vacuum, and after addition of baryta it was agitated with ether. From this ethereal solution, a substance was obtained having an alkaline reaction, a pungent and bitter taste, and crystallising in needles. It gave the general reactions of the alkaloïds, but with platinic chloride it yielded a precipitate only in concentrated solutions. Its reactions with various reagents did not correspond with those of any known alkaloïd. It was found to be poisonous, and free from arsenic and phosphorus. C. E. G.

Formation of Poisonous Alkaloïds in the Human Corpse. By F. Selmi (*Gazzetta chimica italiana*, **9**, 35—37).—As is well known, substances having the general reactions of the vegetable alkaloïds may be extracted from the corpse, some of which are innoxious and others poisonous. The identification of these alkaloïdal substances or *ptomaines* is of great interest to toxicologists, as it is possible they may be confounded with alkaloïds that have been used for the purpose of poisoning.

As it seemed probable that these alkaloïds were produced by the slow putrefaction of proteïd matters, the author enclosed the whites of 60 eggs in a retort, and allowed them to decompose slowly. The product was treated with alcohol, and from the alcoholic solution two basic substances were obtained, one volatile and the other not. The volatile base has an alkaline reaction and a peculiar odour. It forms a crystalline and deliquescent hydrochloride, which gives a turbidity with tannin, and a precipitate with iodised hydriodic acid and with platinum tetrachloride. Gold chloride produces a yellowish crystalline precipitate in solutions of the sulphate. It had no poisonous action on the frog. The non-volatile alkaloïd yields a hydrochloride crystallising in needles, which rapidly undergo change, especially on concentrating the solution. It has a pungent taste, and is poisonous. It gives the general reactions of the alkaloïds and with iodised hydrochloric acid a compound crystallising in long brown needles.

The discovery of a poisonous alkaloïd, soluble in ether, amongst the products of the putrefaction of albumin, indicates the way in which the poisonous ptomaines are formed, and affords a method of obtaining them in quantity sufficient to study their properties. The

author is in hopes, by a careful investigation of the other compounds formed during the slow putrefaction of albumin, to obtain a better insight into the constitution of the proteïds than would be possible by treating them with powerful reagents such as sulphuric acid, baryta, &c. It is, moreover, not impossible that these poisonous alkaloïds, produced by putrefaction, may also be formed in the animal economy when a more or less profound alteration occurs in some of the organs, in the blood, or in the other humours. C. E. G.

Nucleïn from Cow's Milk. By N. Lübawin (*Deut. Chem. Ges. Ber.*, **12**, 1021—1022).—Nucleïn is decomposed by continued boiling with water, a portion of the phosphorus and albumin passing into solution.

If nucleïn is dissolved in a 1 per cent. solution of sodium carbonate, and reprecipitated by dilute hydrochloric acid, it is partly converted into an albuminous compound containing phosphorus, and which is soluble in water.

Caseïn precipitated from milk by acetic acid, is almost completely deprived of phosphorus by long boiling with water. The author considers that phosphorus is present in the same form in nucleïn and caseïn. W. C. W.

Gas Evolved by the Action of Barium Hydrate on Albuminoïds. By L. Liebermann (*Wien. Akad. Ber.*, **78**, [ii], 80—88).—A mixture of dry ox-blood fibrin or egg-albumin with barium hydrate, in proportions of 1 to 5 by weight, was heated in the water-bath, and afterwards in an oil-bath. At 150° nearly pure nitrogen is given off, although in very small quantity, but at a higher temperature, 240—250°, it is mixed with hydrogen and hydrocarbon. The gases were collected over mercury, measured and analysed.

W. S.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Oxygen on Alcoholic Fermentation. By A. Béchamp (*Chem. Centr.*, 1879, 282—284).—Solutions of sugar were fermented by addition of beer yeast, the amount of sugar and of yeast, the time, temperature, and surface exposed being determined in each instance. Two similar experiments were simultaneously conducted; in one oxygen was passed slowly into the fermenting liquid, whilst no oxygen was passed into the other.

In a second series of experiments, oxygen was evolved in contact with the fermenting liquid by placing the electrodes of a battery consisting of 6 to 8 Bunsen cells in the liquid.

The addition of oxygen invariably caused an increase in the amount of alcohol produced in a given time, the vital changes in the yeast proceeding more rapidly when oxygen is freely supplied. The amount of acetic acid produced seems to be dependent more on the quality of

the yeast and the temperature, than on the presence or absence of much oxygen.

In the second series of experiments, the escaping gas, after being freed from carbonic anhydride, contained little or no oxygen. The amount of alcohol was increased by the evolution of oxygen within the fermenting liquid during the earlier stages of the experiments (60—70 hours), but was slightly diminished after the expiration of long periods (14 days); the amount of acetic acid was invariably increased by the evolution of electrolytic oxygen in the fermenting liquid.

Whether the oxygen was absorbed by the sugar or by the yeast remains an unsettled point. Sugar solution without yeast slowly absorbs oxygen for some time, acquiring an acid reaction and the power of reducing alkaline copper solution. Pure yeast suspended in water also absorbs electrolytic oxygen and evolves carbonic anhydride.

M. M. P. M.

Plant Respiration. By E. Freyberg (*Landw. Versuchs.-Stat.*, **23**, 463—470).—The author has investigated, quantitatively, the oxygen-consumption of the roots of land-plants as against aquatic plants of allied species. A comparison of the seed-roots of rice and wheat gave the following results:—

Species.	Length of root.	Temp.	Consumption of oxygen for 24 hours per 1 gram of root substance (dry).
Triticum vulg.....	15·6 mm.	15·3—17·7°	67·9 c.c.
„ „	35·0 „	16·4—18·3	82·8 „
Oryza sativa	14·6 „	14·1—17·1	44·4 „
„ „	27·0 „	16·7—18·1	55·1 „

Upon the results of these and other experiments, also detailed, the author announces for the seed-roots of aquatic plants a maximum oxygen consumption of 56 c.c., and of 38 c.c. for the roots of fully developed plants; whereas the corresponding maxima for land species are 83 and 63 c.c., the numbers having the meaning already assigned. In addition to this direct proof of the lesser oxygen consumption of aquatic plants, which hitherto was an inference merely from the conditions of their life, the author bases the following conclusion upon an extended series of experiments, viz.: that the amount of oxygen consumed by similar plant organs bears a direct relation to the quantity of nitrogen (protoplasm) which they contain. This is shown by the subjoined results:—

	Species.	Nitrogen in dry root substance per cent.	Temp.	O consumption.
Seed roots	*Triticum vulgare*	3·2	15·3—17·7°	67·9
	Oryza sativa	1·6	14·1—17·1	44·4
Leaves ..	*Ranunculus bulbosus*....	4·6	15·4—17·6	29·6
	„ *fluitans*	2·9	17·7—19·0	18·9
„ ..	*Polygonum lapathifolium*	4·6	19·8—21·4	26·6
	„ *amph*.....	3·4	20·3—21·1	21·4
	Glyceria fluitans	1·9	18·3—18·7	11·8

Averaging these numbers expressing the percentages of nitrogen, we obtain, in the case of the leaves (1) of aquatic plants (10 species), 2·92; (2) of land plants (6 species), 4·1. A similar relation holds also for the root substance.

In conclusion, the author regards these results as fully explanatory of the adaptation of aquatic plants to the conditions of a relatively scanty supply of oxygen, and as establishing this in causal connection with their economic inferiority, *i.e.*, with their poverty in nitrogen.

C. F. C.

On the Possibility of Replacing the Carbonic Acid of the Air necessary for the Production of Chlorophyll in Sarcophytic and Parasitic Plants, by Organic Substances. By M. Schmoeger (*Deut. Chem. Ges. Ber.*, **12**, 753—758).—Stutzer (*Ber.*, **9**, 1395) experimented on plants enclosed in vessels, from which the carbonic acid of the air was excluded, and the roots of which were placed in artificial soils containing either calcium oxalate or calcium tartrate; in some cases caustic soda was introduced into the vessels to keep the air free from carbonic acid. From these experiments Stutzer concluded that plants are able by their roots to build up their structures from the organic substances. The author has repeated these experiments, but finds that the growth of the plants is due to the carbonic acid formed by the fermentation of the calcium tartrate and oxalate; and that the growth was small when the air was kept free from carbonic acid, by means of caustic soda. The fermentation of the tartrate is well known. Experiments made with calcium oxalate show that it is decomposed and bacteria appear unless special precaution is taken to prevent their growth; calcium carbonate and carbonic acid are formed thus: $CaC_2O_4 + O = CaCO_3 + CO_2$.

These experiments show that Stutzer's method of investigation is untrustworthy.

P. P. B.

Formation of Nitrites in the Soil. By Grete (*Deut. Chem. Ges. Ber.*, **12**, 674).—The author's experiments do not accord with the statements of Reichardt and Hünefield, that considerable quantities of nitrous acid are formed when air, water, hydrated manganic oxide, and magnesium carbonate are shaken up together. The formation of nitrites is caused by impurities in the materials, even in the filter-paper, and does not take place when pure substances are employed.

G. T. A.

Chemical Composition of the Soils of the Vine Growing Districts of the Rhine and Maine. By A. Hilger (*Landw. Versuchs.-Stat.*, **23**, 447—454).—This paper contains the results of the analysis of the soils of 11 of the more important of the above districts, viz.: Stein Pfülben, Spielberg, Teufelskeller, Schweinfurt, Leisten, Rödelsee, Callmuth, Liebfrauenmilch, Hochheim, and Hörstein. The following may be selected as typical:—

	Stein.	Teufelskeller.	Rödelsee.	Callmuth.	Hörstein.
Loss on ignition ..	3·502	3·451	6·842	2·987	2·461
SiO_2	55·432	12·141	62·857	70·421	60·412
Al_2O_3	7·264	4·621	5·627	2·159	12·612
Fe_2O_3	4·651	3·041	11·879	5·614	2·861
$CaCO_3$	24·430	69·681	7·454	15·613	6·891
$Mg.CO_3$	2·034	5·180	4·362	1·502	0·962
K_2O	0·603	1·241	0·846	0·440	5·142
Na_2O	0·126	0·215	0·204	0·142	4·561
SO_3	0·323	0·006	0·203	0·332	0·002
Cl	0·016	0·014	0·105	0·104	0·102
P_2O_5	0·324	0·815	0·461	0·521	0·264
	98·705	100·406	100·840	99·835	96·360
CaO in combination with silica	0·421	0·026	0·126	0·561	3·412
MgO in combination with silica	0·042	0·015	—	0·021	0·214

The above numbers express the composition of the fine siftings of the soils, obtained by means of a Kolb's sieve. On treating these with hydrochloric acid of sp. gr. 1·08 in the cold for 24 hours, the following constituents were dissolved and estimated :—

	Stein.	Teufelskeller.	Rödelsee.	Callmuth.	Hörstein.
SiO_2	2·142	1·965	4·671	3·418	5·241
Al_2O_3	1·625	1·016	3·167	0·981	4·876
Fe_2O_3	0·956	0·628	6·416	1·876	0·842
$CaCO_3$	24·430	69·681	7·454	15·613	6·891
$MgCO_3$	2·034	5·180	4·362	1·502	0·962
K_2O	0·401	0·641	0·217	0·361	2·601
Na_2O	0·071	0·098	0·098	0·084	2·152
SO_3	0·323	0·006	0·203	0·332	0·002
Cl	0·016	0·014	0·105	0·104	0·102
P_2O_5	0·324	0·815	0·461	0·521	0·264
Per cent. ..	32·322	80·044	27·154	24·792	23·933

The greater portion of these soils are the products of the weathering of the characteristic triassic rocks of the districts in which they occur: in the Hörstein district, on the other hand, the soil has been formed by the weathering of gneiss and hornblende, and is consequently much richer in alkalis; in this respect it may be grouped with those of the Liebfrauenmilch and Hochheim districts, with an average of 8 per cent. of alkalis ($Na_2O + K_2O$).

The grapes of the Stein and Leisten (Schlossberg) districts (October, 1870) were found by the author to yield 1·52 and 1·4 per cent. of ash respectively, the composition of which was as follows :—

	Stein.	Leisten.
K_2O	33·04	34·67
Na_2O	1·84	1·21
CaO	8·55	11·0
MgO	2·61	1·42
Fe_2O_3	1·04	0·45
SiO_2	1·00	0·45
CO_2	22·51	23·78
Cl	2·29	2·03
SO_3	4·54	4·19
P_2O_5	21·08	19·72
	98·50	98·92

The fresh berries were found to yield, when deprived of their water, the following percentages of dry residue:—

Stein.		Leisten.	
1. 12·99		1. 14·70	
2. 14·85	13·98	2. 16·91	15·85
3. 14·09		3. 15·95	

C. F. C.

On the Supply of Nitrogen to Plants. By Heiden (*Landw. Versuchs.-Stat.*, **23**, 399—403).—The results of a series of experiments on the fertilizing action of ammonium sulphate, showed a largely increased yield in the case of cereals, for the manured land (2 lbs. of the salt to the rood, Sax.) as against the unmanured land; leguminous crops on the other hand were unaffected. In the case of a crop of oats, when an interval of a year elapsed between manuring and sowing, and during which the plot was several times dug over, the total yield, grain and straw, was three times as large as that obtained from the corresponding plot of unmanured land. This points to the retention of the ammoniacal salt, unchanged, by the soil.

A second series of comparative experiments was undertaken in order to investigate the question of the mode of assimilation of the nitrogen of the salt. The growth of the rye and vetch, which formed the subject of these experiments, was found, in the earlier stages, to be prejudiced by the presence of ammonium sulphate; the plants grown on the manured plots were fewer and more weakly than those on the unmanured. This condition of the crops was associated with an absence of nitrates, and persisted until about the end of April; a revival of the manured crops was then observed, and appeared to occur *pari passu* with the development of nitrates. C. F. C.

Analytical Chemistry.

Chromometry, an Application of the Blow-pipe to Quantitative Analysis. By G. A. König (*Chem. Centr.*, 1879, 286—287).—A weighed amount of the metallic salt to be determined is fused in a borax bead of known weight; the bead is observed through a glass the colour of which is complementary to that of the bead. Beads containing more than one metallic salt may be employed, provided the colours produced by these salts separately are not complementary. Thus the colour imparted to the borax bead, by a mixture of iron and manganese salts, varies from yellow to red, according to the relative amount of the metals present; if such a bead be examined through a green glass of a certain thickness it appears of a pure yellow colour; if the thickness of the green glass be increased, the colour of the bead appears greenish-yellow; if the thickness be diminished, the bead appears brownish-yellow. The quantities 0·05 mgm. and 0·10 mgm. of Mn_2O_3 in a bead of 100 mgm. of borax mark the limits of greatest delicacy for the manganese reaction.

Details of apparatus are given, but for further explanations reference is made to the original paper (*Proc. Amer. Phil. Soc.*, **18**).

M. M. P. M.

Estimation of Hydrogen Peroxide. By E. Schöne (*Zeitschr. Anal. Chem.*, 1879, 133—158).—1. *Estimation by Permanganate.*—The reaction on which this method depends was first noticed by Brodie, and soon after by Schönbein; it was, however, first quantitatively studied by Aschoff, who proved that the quantity of permanganate solution which was decolorised by a certain weight of ferrous salt, was also exactly decolorised by a quantity of peroxide, which would exactly oxidise the same weight of ferrous salt, provided that the solution always contained free acid. Hence when the permanganate and peroxide react on one another, each gives off an equal volume of oxygen, and the change is represented by the equation—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Brodie confirmed this result by proving that the quantities of permanganate and peroxide which entered into the reaction were equivalent to one another in separating iodine from hydriodic acid. Confirmation was further given by Weltzien, Schrötter, and Thomsen. Hamel and Thenard proved that the volume of oxygen evolved was that represented in the equation, and it was noticed also by Thenard that this oxygen, although freely evolved at ordinary temperatures, was not liberated when the solutions were cooled by a freezing mixture. From neutral peroxide solution, permanganate precipitates manganic and manganous hydrates in varying proportions. Alkaline peroxides, according to Brodie, precipitate manganic oxide from permanganate solution. All the experiments already referred to were made with dilute solutions of peroxide, and therefore only establish the correctness of the above equation in an indirect way. The author's experiments were made with anhydrous peroxide in which the traces of

impurities had been determined, and hence direct proof was obtainable. The peroxide was prepared by decomposing pure precipitated $BaO_2 + 8H_2O$ with dilute sulphuric acid; the solution was evaporated in a vacuum and allowed to stand for some time over the strongest sulphuric acid in a vacuum. A loss of 70 per cent. of the peroxide occurred during this concentration, partly owing to decomposition, but chiefly to the evaporation of the peroxide, its vapour being absorbed by the sulphuric acid. The sp. gr. of the peroxide at 14·8° was found to be 1·4555; Thenard gave the number 1·452. The impurities were determined by evaporating with ammonia, weighing the residue dried at 100°, then igniting and weighing the non-volatile residue. The volatile portion of the residue was considered to be ammonium sulphate and a trace of water expelled from the silicic acid, which thus remained as silicic anhydride in the residue left after ignition. The percentage composition of the peroxide was found to be as follows:—Hydrogen peroxide, 99·10; sulphuric acid, 0·46; silicic anhydride, 0·25; water, 0·19. The author titrated a weighed quantity of this peroxide with permanganate of known strength, and the result fully confirmed the correctness of the equation already given. The permanganate method can be employed volumetrically, as is described above, or the oxygen gas evolved may be measured: v. Hamel prefers the latter method when other substances are present which would decolorise permanganate. The accuracy of the method is, however, evidently interfered with by the difference between the coefficients of absorption of oxygen and of the gases present in the air; calculation shows that in 1 litre of the liquid, the peroxide cannot be estimated with certainty to a milligram. The author prefers to standardise the permanganate solution, either by thin pianoforte wire, or by the double salt, $(NH_4)_2SO_4.FeSO_4.6H_2O$. The salt was obtained of invariable composition by recrystallising several times *at the ordinary temperature*, rapidly washing the crystals with pure water, and placing them in a vacuum over sulphuric acid until they ceased to adhere to each other or to paper; they were then allowed to stand for several days in an ordinary desiccator, and kept in a dry stoppered bottle. Although the solution of this salt is not permanent, the crystals prepared as above are quite unchanged by keeping; further, the percentage of water they contain is always that represented in the formula if they have been formed at ordinary temperatures. When steel wire is employed, the carbon present in the steel does not interfere, as Berthelot supposes, with the titration, since it is all evolved as hydrocarbon during the process of solution. The preparation of pure oxalic acid is certainly more difficult than that of the double salt, and as employed by Berthelot in solution, it is certainly under some conditions not permanent. The process of titration of the peroxide with permanganate is very simple; the solution of peroxide is made strongly acid by adding sulphuric acid, and the permanganate solution is then run in, until the red tint remains; this final reaction is very sharp and unmistakeable, as is proved by determinations of known quantities of the peroxide in different states of dilution: the absolute error was about the hundredth of a milligram, and in a litre, milligrams of the peroxide can be accurately determined, and tenths of milligrams with fair accuracy. An indirect method consists in adding the peroxide

solution to excess of a solution of known strength of ferrous or stannous salt, and then determining the excess of either of these salts by permanganate; the direct method decidedly deserves the preference. The author noticed during these experiments that the peroxide, after exposure to the light, did not at once decolorise permanganate; after the action had once commenced, however, it proceeded with great rapidity, the permanganate being instantaneously decolorised until the end of the titration, and it was further found that after the instantaneous decolorisation which sharply marks the end of the titration had ceased, the purple tint of the liquid slowly became red, and the liquid ultimately deposited brown hydrated manganic oxide, even in presence of free acid. These peculiarities were not noticed if the peroxide had not been exposed to the light, and when it was free from foreign substances, such as barium carbonate, barium bicarbonate, and free alkali.

2. *Determination by Hydriodic Acid.*—The reaction of the peroxide with hydriodic acid is represented thus:—$H_2O_2 + 2HI = 2H_2O + I_2$. Hence this method can be utilised, either by estimating the iodine by standard sodium thiosulphate or sulphurous acid, or by determining acidemetrically the loss of hydriodic acid. Vernon Harcourt has shown that the rate at which the above decomposition proceeds depends on the quantity of peroxide and of hydriodic acid present, other conditions being the same: hence the process will evidently be a slow one when applied to dilute solutions. The author experimented with the method iodometrically, when the decomposition proceeded at ordinary temperature, since the volumetric estimation of iodine is remarkably sharp and accurate; when higher temperatures were used for hastening the decomposition, the acidimetric process was necessarily adopted, on account of the loss of iodine by volatilisation. At ordinary temperatures, the decomposition was complete only after long standing; when there was 1 gram of peroxide per litre of the mixed solutions, nearly 24 hours were required, with ·25 gram per litre, only 98 per cent. was decomposed in 30 hours, and with ·005 gram of peroxide per litre less than three-fourths of the peroxide was decomposed after 48 hours' standing. Of course the process might be hastened by increasing the proportion of hydriodic acid present, but when it is considered that even then the process would be slow, and that hence an error would arise from the decomposing action of atmospheric oxygen on the hydriodic acid, it is evident that in this form the method is by no means to be compared as to accuracy or rapidity of execution with the permanganate method, at least for estimating the peroxide in dilute dilutions. In the experiments made by decomposing at a higher temperature and estimating the undecomposed acid, allowance had to be made for the dissolved atmospheric oxygen present; blank experiments showed that the iodine separated by this dissolved oxygen, and possibly by other causes, was very variable in amount, but might be equivalent very nearly to that separated by 1 milligram of the peroxide per litre: hence the variability and possible magnitude of the error thus introduced renders the method quite inapplicable to the determination of the peroxide in rain, snow, and other atmospheric deposits. Calculation shows that the amount of dissolved atmospheric oxygen present in rain water may be eighteen times as great as the available oxygen of

the peroxide present. It was further found that in dilute solutions the reaction was not complete, and hence a deficiency of peroxide was found. In strong solutions, an excess of peroxide was found, due probably to the error caused by the action of atmospheric oxygen; this excess did not pass the limit of 1 milligram per litre, and hence in strong solutions, where this error would be insignificant, Houzeau's iodo-acidimetric process is applicable.

3. *Estimation by Measuring the Oxygen Evolved.*—This method is employed by Thenard. The solution of peroxide confined in a tube over mercury was decomposed into water and oxygen, either by heat, or by manganic oxide added to the solution freed from acid. Blood-fibrin and blood itself have also been used for separating the oxygen from the peroxide. Brodie effected the decomposition by platinum-black, and weighed the oxygen evolved. The method is inferior in accuracy and facility of execution to the permanganate and iodo-acidimetric processes. Instead of stating results by the volume of oxygen evolved from one volume of the solution, the author prefers giving percentages, or the weight of peroxide contained in a certain volume of the solution. He deduces formulæ for converting results stated according to the former method into either of the latter two.

4. *Estimation by means of Indigo.*—Assmuth and Struve have suggested but not fully developed methods depending on the decolorisation of indigo by the peroxide. Struve found that when mixed with large excess of strong sulphuric acid, and heated with indigo-carmine, 854 parts of the peroxide and 549 parts of nitric anhydride were equivalent quantities.

5. *Colorimetric Method.*—The author has already described his experiments on this process (*Annalen*, **195**, 228); in the present paper the application of the method to the estimation of hydrogen peroxide in atmospheric deposits is described in detail. Iodine is separated by hydrogen peroxide from neutral potassium iodide solution in the presence of starch; and the peroxide is estimated by the intensity of the starch iodide coloration produced. The process is applicable only to solutions containing between ·08 and 1 milligram per litre, but from his experiments in the neighbourhood of Moscow, the author finds that the proportion of peroxide in atmospheric deposits is comprised between these limits; a stronger solution of peroxide might, however, be estimated if previously diluted. The solutions required are (1) a freshly prepared potassium iodide solution, containing ·05 gram in 1 c.c.; (2) starch solution, which may be made about once a fortnight by pouring about 25 c.c. of distilled water upon 1 gram of the best starch in pieces, shaking well, and decanting after the liquid has stood for a minute or two into 400 c.c. of boiling water contained in a flask; the boiling should be continued for a minute or two, and the solution is then kept in the same flask, a beaker being inverted over the mouth to exclude dust; (3) a solution of the purest hydrogen peroxide (which is best prepared as directed in *Annalen*, **192**, 262); commercial hair bleaching liquid may be used, but its free acid must be neutralised by baryta until it does not change the violet colour of neutral litmus. The peroxide present in this solution is estimated by titration with permanganate, and it is then immediately diluted so as to obtain solu-

tions which contain 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9, and 1·0 milligram of peroxide respectively per litre. 25 c.c. of each of these solutions are then measured in a number of carefully cleansed white glass stoppered bottles of 40—50 c.c. capacity; 0·5 c.c. of the potassium iodide solution, and the same quantity of the starch solution are added to each, and after being stoppered and well shaken, the bottles are allowed to stand for five or six hours. In this time the colour becomes fully developed in each, and the series serves for a measuring scale for colour comparison against the test liquids. If well stoppered and kept in the dark, the colours of these liquids remain unaltered for at least a fortnight. If the method is employed systematically at meteorological stations, it would be well to prepare a permanent colour scale. In applying this process to meteorological purposes, the rain, dew, or melted snow or hail is to be filtered, since it is found that the suspended matters impart a more violet tint than that obtained from the pure peroxide, and further they may, if organic, lessen the intensity of the coloration. 25 c.c. are then treated in a manner precisely similar to the peroxide solution used for making the standard coloration liquids; and after standing for five or six hours, the colour is compared with that of the standard bottles. The results obtained by different persons seldom differed by as much as 0·05 milligram per litre when more than 0·8 milligram of peroxide per litre was present, and when the quantity was between 0·08 and 0·40 milligram per litre, hundredths of a milligram per litre can be estimated. Before employing the above method of estimation, the presence of the peroxide should be proved by qualitative tests, such as potassium iodide, starch, and ferrous sulphate or guaiacum resin, and malt-extract, or by chromic acid and ether, or by Struve's test; if the peroxide is thus detected, the absence of chlorine, ozone, nitrous acid, and other substances which would liberate iodine from potassium iodide is proved, since these decompose the peroxide at once.

The author in conclusion points out that this colorimetric method is admirably suited for the estimation of hydrogen peroxide in atmospheric deposits, which seem never to contain more than 1 milligram per litre, the superior limit fixed above. Its results are especially accurate for quantities varying between 0·08 and 0·40 milligram per litre. The permanganate method is also very exact; if the standard solution is accurate, the possible error does not exceed a few tenths per cent. of the total peroxide present, and in dilute solutions milligrams of the peroxide per litre can be accurately estimated, and tenths of milligrams with fair accuracy; it fails when organic substances which affect permanganate are present, and hence is inapplicable for meteorological purposes. Houzeau's iodo-acidimetric method can only approximately measure milligrams per litre, and Houzeau and Brodie's gasometric methods are far inferior in accuracy to the iodo-acidimetric. The indigo method is as yet undeveloped. F. C.

Proportion of Carbonic Anhydride in the Air. By J. Reiset (*Compt. rend.*, **88**, 1007—1011).—Almost all text-books on chemistry contain the statement that the air contains a small quantity of carbonic anhydride, varying ordinarily between 4 and 6 volumes in

10,000. Examination of original memoirs, however, reveals the occurrence of abrupt changes in the quantity of atmospheric carbonic anhydride. In some cases an interval of a few hours under the same meteorological conditions suffices to cause an increase to twice the original amount. Doubting the accuracy of the results hitherto obtained, the author has undertaken a fresh series of experiments. The amount of carbonic anhydride was determined by causing the air, previously dried by passing over pumice moistened with strong sulphuric acid, to bubble through a standard solution of baryta saturated with barium carbonate. Special precautions were taken to ascertain accurately the volume of air that had passed through the apparatus, and to correct for evaporation brought about by the passage of the air through the baryta solution. After allowing the liquid containing the precipitated barium carbonate to stand for forty-eight hours, the clear solution was drawn off, and the unaltered baryta determined by means of standard sulphuric acid.

Two aspirators of 600 litres capacity were employed, one of which was placed permanently in the country, far away from any dwellings, about 8 kilometres from Dieppe. This is called the field station. The air was taken 4 metres from the surface of the ground. The other aspirator was transported from place to place.

Ninety-two determinations made between September 9, 1872, and August 20, 1873, gave on an average 2·942 vols. CO_2 in 10,000 of air. The greatest difference between the maxima and minima was 3 vols. in 100,000. On no occasion was the quantity so high as 4 in 10,000.

The mean of 27 experiments made in a leafy coppice was 2·997 in 10,000. The quantity at the field station at the same time was 2·902.

The air above a crop of red trefoil in flower in the month of June contained 2·898 CO_2 in 10,000. At 0·3 metre above the soil in a barley field in the month of July, the quantity was 2·829. At the field station the amount in the two cases was severally 2·915 and 2·933.

The presence of 300 sheep in the neighbourhood of the apparatus raised the proportion of CO_2 to 3·178 in 10,000.

At Paris, in May, 1873, 1875, and 1879, the mean amount of CO_2 was 3,027 in 10,000.

The author arrives at the conclusion that the atmosphere contains on an average 2·942 vols. CO_2 in 10,000. In very diverse conditions the extreme variations do not exceed 3 in 100,000. C. H. B.

Estimation of Soluble Phosphoric Acid in "Superphosphates." By Wein (*Landw. Versuchs.-Stat.*, **23**, 403—404).—In order to investigate the influence of time in the exhaustion of the soluble phosphoric acid of "superphosphates," portions of 20 grams of a specimen, containing only a small percentage of iron and aluminium oxides, were digested with 1,000 c.c. water in the cold, for 5, 10, and 30 minutes and 2 hours, severally. The quantity of phosphoric acid dissolved in the last case exceeded that in the first by 0·25 p. c.; with this exception no large differences were observed.

The method of exhaustion by means of the filter-pump, a modification recommended by Fresenius and others, the author has found to be

untrustworthy, yielding results varying to the extent of 0·4 p. c. The cause of the variations is to be found in Erlenmeyer's observation of the conversion of mono- into di-calcium phosphate when treated with a small quantity of water (except in the presence of free acid).

The author is therefore of opinion that it is not expedient to depart from the ordinary method, as regards length of time and quantity of water; but that the filtration method is admissible in cases where the specimen contains free acid. C. F. C.

Estimation of Cadmium. By F. Beilstein and L. Jawein (*Deut. Chem. Ges. Ber.*, **12**, 759—762).—The cadmium compound is converted into nitrate, neutralised with caustic potash, and potassium cyanide is added until the precipitate is dissolved. The solution diluted so that 75 c.c. contain about 0·2 gram cadmium, is then placed in a beaker and surrounded with a vessel containing cold water, and into it a platinum electrode introduced similar to that used in estimation of zinc (*Ber.*, **12**, 447). Three Bunsen cells, the zincs of which are 15 cm. high, are used to precipitate the metal, which is deposited at the rate of 80—90 mgms. an hour. The metal, which forms an adherent mass, is washed with water and alcohol. It is finally dried by bringing it into a hot platinum basin, and is then weighed. In this manner the authors have obtained very accurate results. P. P. B.

Electrolytic Estimation of Cadmium. By E. F. Smith (*Am. J. Sci.* [3], **17**, 60).—The estimation of cadmium by electrolytic deposition from solutions of the chloride gives inaccurate results, as the precipitated metal retains impurities, but a satisfactory determination may be made with solutions of the acetate, when the cadmium is deposited as a crystalline greyish-white layer. With two Bunsen or dichromate cells, the process is complete in about three hours. The precipitated metal is washed with water, then with alcohol, and lastly with ether, and dried over sulphuric acid. The author advises that a rather concentrated solution should be employed, and also a sufficient number of cells to give a rapid and energetic current. C. H. B.

Estimation of Manganese. By C. Rössler (*Deut. Chem. Ges. Ber.*, **12**, 925—928).—This method is based on the observation of Wöhler (*Pogg. Ann.*, **41**, 344), that a compound having the composition $Ag_4Mn_2O_4$ is precipitated when an alkali is added to a mixture of silver nitrate and a manganous salt.

The solution containing the manganese as a manganous salt, and from which the chlorides, bromides, iodides, and cyanides, and also those organic compounds which reduce silver salts, have been removed, is brought into a half or quarter litre flask and mixed with an excess of a decinormal solution of silver nitrate. The mixture is heated on a water-bath, and sodium carbonate is added until the silver is completely precipitated.

10 c.c. of ammonia (sp. gr. 0·958) are now added for every 50 c.c. of silver nitrate used. The flask is cooled, filled with water, and its contents after having been well shaken are filtered. The quantity of silver contained in a measured volume of the filtrate is determined by

Volhard's process with potassium thiocyanate. From these data the volume of silver nitrate solution required for the precipitation of the manganese can easily be calculated; each c.c. corresponds with 0·00275 gram of manganese. If the substance contains iron, it must be converted into a ferric salt. To determine the manganese in a sample of iron, the metal is dissolved in nitric acid (sp. gr. 1·2), the solution is neutralised with sodium carbonate, and the iron precipitated by boiling with sodium acetate. The mixture is cooled, diluted to half a litre, filtered, and the manganese estimated, as above, in the filtrate. The object of precipitating the iron with sodium acetate, is that organic compounds which would reduce the silver are carried down with it and removed from the solution. W. C. W.

Fractional Combustion of Hydrogen and Marsh-Gas. By W. Hempel (*Deut. Chem. Ges. Ber.*, **12**, 1006—1008).—When a mixture of hydrogen, marsh-gas, and air is passed over spongy palladium at the ordinary temperature, the hydrogen combines with the oxygen to form water, but the marsh-gas undergoes no change until the temperature reaches 200°.

The author proposes to estimate the amount of hydrogen in a mixture of gases by measuring the contraction which takes place when the gas mixed with air is passed over spongy palladium.

W. C. W.

Chloroform as an Anæsthetic. By J. Regnauld (*J. Pharm.* [4], **29**, 402—405).—The purity of chloroform for anæsthetical purposes being very important, the following simple tests are recommended by the author.

If chloroform is dropped on paper and allowed to evaporate, the last portion on being inhaled has a characteristic pleasant smell, and leaves the paper perfectly dry and odourless; impure chloroform however possesses a disagreeable irritating odour, which it imparts to the paper.

Pure chloroform does not redden blue litmus or give even a cloudiness with silver nitrate. If it should do either, it contains hydrochloric acid or the products of decomposition of some other chlorides.

Pure chloroform remains perfectly colourless when boiled with potash; the presence of aldehyde causes a brown coloration.

When shaken with concentrated sulphuric acid and allowed to stand for half an hour, the two liquids should separate into two colourless layers. The presence of alcoholic chlorides produces a brown coloration.

The purity of chloroform may be judged by its constant boiling point, 60·8°. Impure chloroform may boil above or below according to the impurities it contains.

The sp. gr. of chloroform can hardly be used as a criterion of its purity, since its determination has been attended with conflicting results. Liebig has found the sp. gr. of pure chloroform to be 1·48 at 18°. Suberain (*ibid.* [3], **16**, 5) shows that this number is too low, the sp. gr. at 12° being 1·496. Again, Remys (*Arch. Pharm.* [3], **5**, 31) points out that the sp. gr. of pure chloroform is 1·5 at 15°, and moreover the presence of $\frac{1}{800}$ of alcohol lowers the sp. gr. ·002.

The purity of chloroform may to a certain extent be judged by the complete insolubility of Hoffmann's violet in it: if it contains a trace of alcohol, the solution is coloured a beautiful purple.

L. T. O'S.

Reaction of Salicylic Acid with Ferric Salts. By S. Pagliani (*Gazzetta chimica italiana*, **9**, 23—26).—As it is well known that the presence of mineral acids interferes with the colour reaction obtained with ferric salts and salicylic acid, the author determined to study quantitatively the effect of sulphuric, nitric, and hydrochloric acids. He finds that the larger the quantity of water present, the larger is the amount of acid required to destroy the violet colour, so that when water is added to a solution which has been only just decolorised by an acid, the violet tint reappears: an excess of ferric salt also renders the test more sensitive. With respect to the amount of acid which will prevent the production of colour reaction, this differs for the three acids, requiring about 400 times the weight of the salicylic acid for sulphuric acid, 385 times the weight for nitric acid, and only 36 times the weight for hydrochloric acid, with the same quantity of water (1 gram or less of salicylic acid per litre). It is advisable in employing Robiquet's method for detecting salicylic acid in urine, to take the precaution not to add too much lead acetate, so as not to have a large quantity of free acetic acid, and also to avoid adding excess of sulphuric acid.

C. E. G.

Separation and Estimation of Hippuric Acid. By P. Cazeneuve (*J. Pharm.* [4], **29**, 309—311).—The author reviews his method for the separation and estimation of hippuric acid (*J. Pharm.*, Sept., 1878), giving examples, and points out that it is necessary to add yeast to diabetic urine to destroy the glucose which seriously interferes with the method. Another method for the extraction of hippuric acid is to pass chlorine through the urine, when hippuric acid separates out on cooling the solution; the acid may be purified by crystallisation. It is important that the urine should not be alkaline, otherwise benzoglycollic acid is formed. This method, although inapplicable for the estimation of hippuric acid, affords a ready means for obtaining it in colourless crystals.

L. T. O'S.

Characteristic Reactions of Picrotoxin and of some of its Derivatives. By A. Oglialoro (*Gazzetta chimica italiana*, **9**, 113—118).—The close resemblance between the physical properties of picrotoxin and those of hydrate of picrotoxide induced the author to compare the reactions of the two substances, and also to examine the behaviour of bromopicrotoxide with different reagents. After noticing the known reactions of picrotoxin, the comparative experiments made with picrotoxin, and its derivatives are described in detail.

Reaction with Nitric Acid and Potash.—When a small quantity of nitric acid is added to picrotoxin and the mixture carefully evaporated to dryness, a yellowish-red amorphous residue is obtained which slowly dissolves in potash with a bright red colour. Hydrate of picrotoxide treated in the same manner with nitric acid yields a crystalline residue, which dissolves in potash with a brilliant red

colour; this, however, disappears rapidly, leaving the solution colourless. If the liquid is evaporated to dryness, acidified with hydrochloric acid, and ferric chloride is added, it becomes of a bright yellow. Bromopicrotoxide gives a yellow and not a red coloration with nitric acid and potash.

Reaction with Picric Acid.—On mixing a 2 per cent. solution of picric acid with potash and heating, an orange-coloured solution is obtained which deposits crystals of the potassium compound on cooling. If, however, picrotoxin or hydrate of picrotoxide be added to the solution, the colour is very much deeper, and on cooling no crystals are deposited. The presence of bromopicrotoxide produces none of these effects.

Reaction with Fehling's Solution.—On dissolving picrotoxin or hydrate of picrotoxide in dilute potash, adding a few drops of Fehling's test and heating, reduction takes place. Bromopicrotoxide has no action.

Reaction with Chromic Mixture.—When a few drops of concentrated sulphuric acid are poured on to picrotoxin or hydrate of picrotoxide, it dissolves with a yellow colour, passing into saffron-yellow: the addition of a small quantity of potassium dichromate in powder changes this to greenish-violet, which on diluting with water passes into greenish-yellow. Bromopicrotoxide dissolves in sulphuric acid, yielding a colourless solution which becomes yellow on adding potassium dichromate.

Reaction with Potash.—Both picrotoxin and hydrate of picrotoxide when added even in minute quantity to potash solution, colour it yellow, but this soon disappears. If the solution be now heated on the water-bath the coloration is reproduced, becomes yellowish-red, and then bright brick-red, and finally if heated over the bare flame it acquires a brown tint. Bromopicrotoxide gives no reaction with potash in the cold, but on heating, colour changes occur similar to those just mentioned.

Reaction with Copper Acetate.—When picrotoxin or hydrate of picrotoxide is carefully heated to boiling with a dilute solution of copper acetate, a turbidity is produced and a black pellicle is formed, the liquid becoming colourless. Bromopicrotoxide likewise produces the black deposit, but the liquid does not become decolorised.

Neither picrotoxin nor hydrate of picrotoxide gives any reaction with gold, platinum, or mercury chloride, or with tincture of iodine, or with tannic acid. C. E. G.

Milk from Cows of different Races. By E. Marchand (*J. Pharm.* [4], **29**, 311—318).—The milk analysed, 62 specimens in all, was obtained from 18 different breeds of cows. The results of the analyses are detailed in the paper. In normal milk, the author invariably finds free lactic acid, the quantity varying from 0·82 to 4·22 grams per litre. When lactic fermentation sets in, it commences slowly, and increases in rapidity until the milk coagulates, which it does spontaneously when the quantity of acid present is from 7 to 8 grams per litre. The fermentation then proceeds more slowly until the acid amounts to 12 to 13 grams per litre. In all cases, the lactic acid formed represents in the state of hydrate the weight of lactose de-

composed, whilst the anhydrous acid amounts to $\frac{9}{10}$ of the weight of the sugar. By neutralising the acid as it is formed, the total quantity of lactose can be estimated as lactic acid by separation as zinc lactate, and decomposing the latter with oxalic acid, when lactic acid is obtained.

To estimate the free lactic acid in milk, it is coloured with an alcoholic solution of turmeric, and titrated with a solution of caustic soda, capable of neutralising half its volume of a solution of crystallised oxalic acid, containing 70 grams per litre, which is equivalent to 90 grams anhydrous lactic acid, or 100 grams hydrated acid. 25 c.c. of the milk are shaken with an equal volume of water and titrated with the soda solution, each c.c. of which corresponds with 0·08 gram lactic acid, therefore the volume of soda solution used, 0·05 × 40 (25 c.c. = $\frac{1}{40}$ litre), gives the weight of free lactic acid per litre contained in the milk.

The author has classified the milk from different cows according to their richness in lactose, lactose and lactic acid, and proteïds.

(1.) Milk which has not undergone lactic fermentation contains from 50 to 54 grams of lactose per litre, and as an exception it reaches 58 grams.

(2.) The quantity of proteïds seems to vary between 19 and 28 grams per litre, but never exceeds the latter quantity.

It is necessary always to determine the free lactic acid in milk, from which it is easy to deduce the quantity of lactose originally contained in the milk. L. T. O'S.

Technical Chemistry.

Heliographic Printing. By A. Ott (*Dingl. polyt. J.*, **231**, 349—357).—Heliographic printing is a photo-mechanical process, whereby a film of gelatin rendered sensitive to the action of light by a chromium salt serves as a press-plate, from which a number of copies may be printed in lithographic presses. The prints obtained are not only equal in sharpness to the best photographs, but surpass them in durability and cheapness, and possess the advantage that they are ready for use when taken out of the presses, without requiring further treatment. Thick plate-glass plates are used, which are treated with the following mixture. 30 parts of egg-albumin are made into a froth, and 25 parts of water, a concentrated solution of 1 part of potassium dichromate, and 10 parts of ammonia, are added. The mixture is filtered and then spread over the glass, taking care to avoid the formation of bubbles in pouring the solution on to the glass. The plate is then dried in the dark at the ordinary temperature. When dry the prepared side of the plate is placed on an even surface, which has been covered with a black cloth. It is now exposed to the action of diffused light until the film is no longer "tacky" when touched with the moist finger. For the film of the picture, the follow-

ing solution is prepared:—10 parts of isinglass are soaked in 15 times the weight of water for 2 to 3 hours, and 40 parts of gelatin in 10 to 12 times the weight of water for one hour. Both these substances are then dissolved by gentle heat, mixed, and treated with a solution of $12\frac{1}{2}$ parts of potassium dichromate. The mixture is filtered, enough ammonia having been added to produce a yellow colour, so as to avoid the spontaneous change of the film. The mixture is then poured over the above coating, the plate having been previously warmed to 40°, and it is dried at 50°. With regard to the exposure of the plate the following data are given. The negative is placed with its picture side on the prepared layer, fixed in a copying frame, the operation being performed in yellow light on a black cloth to avoid all reflection of rays of light. The time for exposure varies with the negative used: ordinary *clichés* require about $\frac{1}{4}$ of an hour in the sun and $1\frac{1}{2}$ hours in diffused light. After exposure the plate is washed with well-water until free from uncombined chromium. It is then treated with a 1 per cent. solution of alum, again washed, and finally dried. In order to be able to copy any number of prints without having to moisten the plates, the so-called "etching" process may be adopted. The following mixture is used, which is said to keep the plates wet for a considerable time: 150 parts glycerin, 50 parts solution of ammonia, and 5 parts of potassium nitrate in 25 parts of water.

The great secret in heliographic printing is the choosing of gelatin of a good quality, the main requisite being resistance to mechanical pressure.

Heliographic Printing on Sheet-Zinc.—The plates employed are those used in hot-pressing paper. They are treated once or twice with a 3 per cent. solution of chromic acid, chromate of zinc remaining on the surface in the form of a yellow powder, which adheres firmly to the plate, and produces the combination between the gelatin and the metal. The plate after being well washed with water, is treated with a hot filtered solution of gelatin containing 1 part gelatin, 20 parts water, and 4 parts alcohol. It is then dried at 45—55°.

Photographs printed with vitrifiable pigments have been recently used for burning in on porcelain, glass, and stoneware. The process is a very ingenious one. Pyroxylin or paper nitrated in another way is printed from the photograph, and in the place of ordinary printing varnish a varnish is used consisting of a vitrifiable pigment and an oil, which when heated volatilises completely. The nitrated paper, which before being printed has been painted with starch, is moistened with water or very weak nitric acid, and pasted on the porcelain or glass to which it is to be transferred, and after being allowed to dry is fired in the usual manner: the paper is consumed completely without damaging the colours, while a sharp picture remains on the vessel. D. B.

Soda Industry. By G. Lunge (*Dingl. polyt. J.*, **231**, 337—349, and 443—445).—In this paper, Leblanc's process and the improvements recently made by Péchiney and Weldon are more fully discussed. It is a well-known fact that potassium cyanide is formed in the soda-fusion process, and that this compound plays an important part in alkali making, since it is impossible to obtain a white product

from the crude soda-liquors on evaporation. The potassium cyanide is converted into potassium ferrocyanide, which cannot be removed from the lyes. On calcining the residue, ferric oxide is formed, which imparts a yellow colour to the product.

Péchiney's process of remedying this defect is based on the assumption that the formation of cyanogen compounds takes place in the black-ash furnace towards the end of the operation, when the sulphate has been decomposed almost completely, and is greater at a lower temperature than at a higher one. It may, however, be prevented by conducting the heating operation at as high a temperature as possible, and adding towards the end of the process a fresh quantity of sodium sulphate, which destroys any cyanide that may be contained in the charge. It is also recommended to work with a minimum of mixing coal.

Weldon, who introduced Péchiney's process in England, has improved the same by adding limestone-dust to the charge towards the end of the operation together with Péchiney's additional sulphate, the object being to free the nearly finished product from sodium sulphide and to obtain a purer soda.

In *Chem. News*, **38**, 130, Mactear states that the formation of the cyanogen compounds takes place towards the end of the balling process, when a higher temperature prevails, and that such compounds are formed in the black-ash furnace more readily, and in greater proportion at high temperatures than at lower ones. Weldon contradicts this statement, and adduces the following facts:—(1.) By working with a lime-sludge containing about 50 per cent. of water, the temperature of the furnace is always lower, and the quantity of cyanides greater than when a limestone mixing has been used. (2.) A revolver heated with gas gave a product containing five times the ordinary proportion of cyanogen compounds obtained when the firing is done with coal, the heat being greater in the latter case. (3.) Hand-furnace black-ash contains less cyanides than black-ash from revolvers, the former being usually worked at a higher temperature. (4.) In France black-ash furnaces are worked hotter, and the melt kept in the furnaces longer, than in England, nevertheless the product contains a smaller amount of cyanides. (5.) Since it has been found necessary in England to work with but little mixing coal, and to use a very high temperature to obtain the best possible black-ash, it has been observed that black-ash contained less cyanides when worked in revolvers at high temperatures than that made at lower temperatures under exactly the same conditions. (6.) If limestone-dust is added in sufficient quantity to carry the cooling effect beyond a certain degree, more cyanogen compounds are found in the product. It is therefore best not to allow the quantity of limestone-dust added to exceed a certain limit.

In answer to these data, Mactear declares (*Chem. News*, **38**, 162) that the formation of cyanogen compounds depends on the melting point of the mass and not on the temperature of the furnace; if the former is high, a larger proportion of cyanides is produced, not from the nitrogen of the mixing coal, but from the nitrogen of the air. Weldon replies in a paper printed for private circulation in a very

energetic manner, disputing Mactear's statement. To prove that cyanides are formed in the black-ash furnace from the nitrogen of the mixing coal, Weldon mentions the fact, that a German alkali manufacturer used an exceptionally nitrogenous mixing coal, and obtained a product so rich in cyanides that he found it advantageous to separate the ferrocyanide by crystallisation. Another portion of the cyanogen compounds is undoubtedly formed from the nitrogen of the firing coal existing in the furnace-gases as ammonia, whilst the nitrogen of the air has extremely little, if any, part in the formation of these bodies.

Weldon mentions that white-ash may be obtained by using as much as 60 per cent. of mixing coal, removing all cyanides by Péchiney-Weldon's final addition of sodium sulphate and limestone-dust. French manufacturers have been accustomed to obtain a white soda by diminishing the quantity of mixing coal and leaving a portion of their sulphate undecomposed. Péchiney, however, found that the whole of the sulphate could be decomposed by combining the diminution of the mixing coal with—what is the exact opposite to Mactear's views—a temperature higher than usual at the finish and a longer exposure.

Schofield's furnace has been improved by Mactear, and is now very largely used for calcining purposes, the advantage being that by a mechanical construction of the furnace large quantities of ash can be calcined with a small amount of fuel, the product moreover being whiter than that usually obtained.

A great improvement in the Leblanc process will have been made if Schaffner and Helbig's method of working up the lixiviated residues gives the same results when worked on a larger scale as heretofore. The process is based on a series of ingenious reactions, by which the whole of the sulphur is recovered in conjunction with the lime contained in the residues, the latter being reduced to a small volume. The residues are then treated with magnesium chloride, when the following reaction takes place: $CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S$. The precipitate is freed from coke or other impurities, and the purified mixture of magnesium oxide and calcium chloride is treated with carbonic acid to convert it into magnesium chloride and calcium carbonate. The former is again used for the first operation of the recovery process, whereas the latter is dried and used in the soda-fusion. About one-third of the sulphuretted hydrogen escaping in the first treatment is burnt, and the sulphurous acid given off allowed to act on the remaining gas, sulphur and water being produced. This reaction has been tried repeatedly on a large scale, without giving satisfactory results, since a large quantity of pentathionic acid is always produced. Schaffner and Helbig found that in the presence of neutral salts the formation of this acid is prevented.

The residual liquors may also be treated with sulphurous acid and decomposed with hydrochloric acid according to Mond's method. Another process is to mix them with oxides of iron, manganese, or calcium, and to burn the metallic sulphides formed.

As a supplement to the above paper, the author mentions the new discovery by Schlösing of a method of separating vapours from gases or other vapours mixed therewith. Hitherto it has always been

assumed that the most advantageous circumstances for condensing, *e.g.*, hydrochloric acid gas, is to cool it as much as possible; this Schlösing believes to be erroneous. He states "that the cooling diminishes the vapour tension of the bodies suspended in the surrounding medium, so that they alone, in consequence of the mechanical current, are slowly brought in contact with the agents of absorption, whilst on the other hand, if the tension is considerable, the absorption causes a continuous current of the volatile body to the absorbing surface." Schlösing therefore recommends that the bodies to be absorbed should be kept at such a temperature as to retain a certain degree of vapour tension. The absorption is thereby promoted, and the condensing apparatus simplified and diminished.

The author doubts the correctness of this discovery, and states that it can only mean that solids or liquids in a stream of gas should be converted into the gaseous form by an increase of temperature, so as to establish a current towards the surfaces of absorption. This cannot apply to hydrochloric acid, as the effect of cooling it does not deprive the gas of its tension, for this at + 10° still amounts to 40 atmospheres. D. B.

Composition and Durability of Glass. By R. Weber (*Ann. Phys. Chem.* [2], 6, 431—450).—The qualitative properties of good and bad glass are detailed at some length. Good glass is unaltered by long continued exposure to the atmosphere, while the surface of bad glass is more or less rapidly rendered uneven; dust adheres easily to bad glass, but not to good, &c.

The glasses examined all contained very small quantities of alumina; they comprised specimens of window glass, glass for optical instruments, for mirrors, for shades, and clock glasses. Many analyses are detailed. The general result is that in good glass the proportion of silica to lime and alkali (potash or soda) is $6SiO_2 : 1CaO : 1 \left\{ \begin{matrix} K_2O \\ Na_2O \end{matrix} \right.$.

If more than one equivalent of alkali be present, the amount of silica must be increased beyond six equivalents; if there be less than six equivalents of silica, the amount of alkali in proportion to lime must be reduced to less than one equivalent. If the alkali be potash, a small increase beyond one equivalent causes a greater deterioration in the glass than if soda be the alkali present.

In good window glass, the proportion of lime to alkali generally exceeds 1 : 1 equivalent; such a glass is brilliant and lustrous. Glass which is to receive a high polish, on the other hand, must be somewhat rich in alkali, and therefore necessarily also in silica; such a glass is harder than window glass.

In bad glasses, there are generally somewhat less than three equivalents of silica to one of base (lime and alkali), and also more (sometimes as much as eight or nine times more) than one equivalent of alkali to one of lime.

A few lead glasses were examined. Good lead glass seems generally to contain silica, lead oxide, and alkali approximately in the proportion of $3SiO_2 : 1PbO : 0{\cdot}3 \left\{ \begin{matrix} K_2O \\ Na_2O \end{matrix} \right.$. If the proportion of lead oxide to alkali

much exceeds 1 : 0·3, or if that of silica to the base falls below 3 : 1, the glass does not long withstand the weathering action of the atmosphere. Further analysis of glasses rich in alumina are promised.
M. M. P. M.

Extraction of Silver from the Fahl-ores of Baranca, Mexico. (*Chem. Centr.* [3], 1878, 830—831).—The fahl-ore, containing zinc-blende, galena, iron and copper pyrites, quartz, silver, and a trace of gold, was crushed and roasted with 5 to 7 per cent. of salt. The copper and zinc were then extracted by treatment with cold water, and the copper precipitated from the solution by iron. From the insoluble residue the silver with a little lead was extracted by solution of sodium thiosulphate, and the silver precipitated by calcium sulphide. This precipitate when roasted gave a metal of 650—700 thousandths fineness, which was purified by cupellation with lead. F. C.

Preparation of Manganiferous Pig-iron. By P. Jordan (*Dingl. polyt. J.*, **231**, 427).—At the iron foundry of St. Louis, near Marseilles, ferromanganese has been produced for several years containing as much as 87·4 per cent. manganese. Recently some peculiar observations were made with regard to the behaviour of manganese in the blast furnaces. The total quantity of manganese found in the ferromanganese and slag produced, is never equal to that contained in the ores, the difference being about 10 per cent. Experiments were made which proved that at the temperature of the blast-furnaces manganese is volatile. Other metals probably behave in a similar manner. Moreover in casting alloys containing readily fusible metals luminous gases characteristic of these metals are often observed on the surface of the fluid. D. B.

Enamel for Cast and Wrought Iron. By T. Raetz (*Chem. Centr.* [3], 1878, 800).—A glassy, transparent, and strongly adherent enamel is obtained by powdering a fused mixture of 130 parts of finely powdered lead glass, with 20·5 of calcined soda, and 12 of boric acid. Layers of different fusibilities may be used; the ground-layer which is first placed on the iron is imperfectly fusible; it is made by fusing together 30 parts of finely-powdered felspar and 25 of borax, and mixing the powdered mass with 10 parts of clay, 6 of felspar, and 1·75 of magnesium carbonate. This is mixed to a paste with water, placed on the surface to be enamelled, and over it is scattered the more fusible powder made by fusing 37·5 parts of quartz powder, 27·5 of borax, 50 of tin oxide, 15 of soda, and 10 of saltpetre. The evenly spread layer is carefully dried and melted in a muffle-furnace. F. C.

A New Application of Rapid Oxidation by which Sulphides are Utilised for Fuel. By J. Hollway (*Tr. Soc. Arts*, February, 1879).—When air is blown into molten ferrous sulphide, oxidation proceeds rapidly in accordance with the equation: $FeS + O_3 = FeO + SO_2$, and much heat is evolved. The author utilises this reaction by melting iron pyrites along with coke in a cupola furnace, transferring the molten ferrous sulphide to a Bessemer converter, turning

on the blast, and from time to time throwing in charges of pyrites and sandstone. In this way, large quantities of pyrites are oxidised without the use of fuel other than that required to heat the blast. A siliceous slag is produced, a quantity of mixed slag and regulus, and a regulus containing nearly the whole of the copper, silver, and gold present in the original pyrites. Preliminary experiments show that the process is of wide application. The special form of plant to be adopted has not yet been determined: the Bessemer converter was employed only in preliminary trials. The pyrites and sandstone may be thrown into the vessel in lumps.

The author's experiments establish the following points:—

When air is blown into a thin stratum of molten ferrous sulphide, the whole of the oxygen is utilised for oxidation.

Pyrites being thrown in, as already described, about one-half of the sulphur contained therein is expelled in the free state, along with the more volatile metallic sulphides, *e.g.*, lead and arsenic sulphide present in the pyrites. It will be possible so to arrange the plant that this sulphur may be condensed and removed.

The remainder of the sulphur, about 20 per cent. in all, with the exception of that found in the regulus, is principally evolved as sulphurous anhydride. The regulus generally contained about 22 per cent. of sulphur; the pyrites about 33 per cent. About 14 per cent. of the escaping gases consists of sulphurous anhydride, the remainder being nitrogen. The sulphurous anhydride may of course be utilised in the manufacture of sulphuric acid; or it might be condensed in coke towers.

In the ordinary method of burning pyrites, although about 45 per cent. of the sulphur is oxidised, the gases produced only contain about 16 per cent. of sulphurous anhydride and 84 per cent. of nitrogen.

If an excess of iron sulphide be always present, copper, silver, gold, nickel, and certain other metals are all concentrated in the regulus. Even if these metals be added in the form of oxide or silicate, it is very probable that these compounds will be converted into sulphide, and that the metals will be concentrated in this form in the regulus. If this be proved experimentally, the process will be suitable for working poor copper ores, slags containing copper, silicates of nickel, &c.

The slag consists chiefly of ferrous ortho-silicate, generally containing traces of copper, small quantities of lead, zinc, &c., and a few per cent. of sulphur. Inasmuch as the slag is perfectly fused, but small quantities of copper only are entangled therein. The small difference between the specific gravity of the slag and that of the regulus (average 4·1 and 4·8 respectively) prevents the complete separation of the latter.

The author is, however, of opinion that he will be able to add more silica than he has yet done, and so produce a lighter slag. As the slag contains from 40 to 50 per cent. of ferrous oxide it might be used in the Bessemer process or otherwise utilised.

The exact character of the lining to be employed for the furnace must be regarded as yet unsettled: if sufficient silica be added to produce a slag containing more silica than required by the formula

$(M''O)_2SiO_2$, the molten slag exerts little or no corrosive action on a siliceous lining.

Calculations are given of the cost of proposed plant, of fuel, &c. The applicability of the process to the treatment of the Spanish ores *in situ* is pointed out.

In one experiment a peculiar slag was obtained, agreeing with the formula $13FeO.FeS.7SiO_2$: this ferrous sulpho-silicate had a sp. gr. of 4·2, a metallic appearance, and crystallised in confused groups of prisms. M. M. P. M.

Extraction of Copper by Wet Processes. By F. Bode (*Dingl. polyt. J.*, **231**, 254—265, 357—362, and 428—436).—From his studies of the preparation of copper in the wet way since 1865, the author is in possession of a complete literature regarding the various methods. The following are the main points considered:—

I. Obtaining the copper in the soluble form. II. Extracting the soluble copper salts. III. Treating the lyes. IV. Precipitating the copper. V. Treating the products and residues.

I. *Converting the Copper into the Soluble Form.*—1. Extraction by means of water takes place gradually in nature by the formation of cement-water in the weathering. This water often contains as much as 0·28 kilo. of copper per cubic meter. A more rapid mode of obtaining the copper, however, is that of roasting cupriferous ores previous and subsequent to their lixiviation. De la Rue and Müller mix ground burnt pyrites with sulphuric acid, form the mass into blocks, and heat it, so that iron sulphate is decomposed; the undecomposed silver and copper sulphates are then extracted by water.

Hauch's process depends on the treatment of residues containing copper, silver, and gold (also small quantities of lead) with sulphuric acid of 60° in cast-iron pots, boiling the mixture until it thickens. Copper and part of the silver form soluble sulphates (the part of silver alloyed with gold being insoluble). The silver is separated by means of sodium chloride, and from the solution, the copper is precipated by iron.

2. *Extraction with Acids.*—The ores must contain as little lime or substances absorbing acid as possible. The various methods of extracting copper from ores or residues by means of hydrochloric and sulphuric acids are fully described in this section. Fitzgerald obtains copper (and other metals) from the ores by treatment with nitric acid, and passing air through the warm mixture. With regard to the methods of desilvering copper obtained in the wet way, the argentiferous and auriferous metal is moistened with warm sulphuric acid, copper sulphate being formed and removed in the usual manner: the residue, besides silver and gold, also contains lead, antimony, and arsenic. To prevent the production of copper sulphate in this process, the following treatment has been proposed. Calcining the copper, grinding and sifting the oxide, roasting with iron sulphate or pyrites, so as not to decompose the silver salt formed, but to decompose the copper sulphate. Lixiviating the silver salt with warm water, according to Ziervogel (and if the residues are still rich in silver, roasting with sodium chloride and extracting the silver salt with a hot solution

of salt, according to Augustin's method), and adding the exhausted residues to the dry copper.

Kerpely recommends the use of a cold solution of sodium chloride, which is said to possess as great a solvent power for silver chloride as a warm solution, the advantage being that it dissolves less chlorides of lead and antimony.

3. *Extraction by Chlorinating.*—(*a.*) Chlorination in the dry way by roasting with sodium chloride. Henderson's method.—The burnt ores are crushed, mixed with salt, and roasted in ovens at low temperatures. The mass is lixiviated with the final liquors of a previous operation, then with hot water, and finally with dilute hydrochloric acid obtained in the roasting and condensed in towers. The copper in solution is thrown down by iron.

(*b.*) Chlorination in the wet way. Kopp's method.—The property which iron chloride possesses of giving up chlorine readily and forming a powerful chlorinating and oxidising agent (the chlorine combining with the hydrogen of water) is made use of in this process. The method is described in *Dingl.*, **199**, 400.

Sterry Hunt and Douglas extract by means of ferrous chloride and sodium chloride. The following is the principle on which their method is based. Ferrous chloride is decomposed by cuprous oxide, cupric oxide, and copper, thus, $2FeCl + 3CuO = CuCl + Cu_2Cl + Fe_2O_3$; $2FeCl + 3Cu_2O = 2Cu + 2Cu_2Cl + Fe_2O_3$. Cuprous chloride, although insoluble in water, dissolves in a hot solution of salt. If the reactions take place at the same time, the separated copper is redissolved, thus, $CuCl + Cu = Cu_2Cl$, the result being a complete solution of the copper in the form of cuprous chloride. By cementation with iron the original solvent is regenerated thus: $Cu_2Cl + Fe = 2Cu + FeCl$.

(*c.*) Chlorination in the dry and wet way. Stella patented a method for extracting copper from burnt pyrites by roasting the ground residues with sodium chloride and digesting with sea-water and sulphuric acid.

4. *Extraction by Means of Ammonia.*—Ammonia, ammonium carbonate, or other salts of ammonium, form with the oxide and the carbonate of copper double compounds, from which the metal may be separated as sulphide by barium or calcium sulphides.

5. *Fluxes other than Sodium Chloride.*—Monnier recommends the use of soda, and afterwards of sodium sulphite, in roasting copper pyrites ores. According to the Snowdon process, the ores are mixed with slacked lime, formed into bricks, and roasted, the copper sulphate being separated in the usual manner, and the metal precipitated as sulphide.

Other methods of less importance are mentioned in the original paper.

II. *Lixiviating the Soluble Copper Salts.*—This is done either by filtration and pressure or by agitation. The vessels used are wooden vats with a false bottom, provided with perforated clay plates, covered with a filter of coke or other material. The liquors are transported by means of elevators or montejus.

III. *Treating the Liquors.*—1. *Removing the Impurities.*—In order to

separate antimony and arsenic from the acid liquors obtained in working up burnt pyrites ores, according to Henderson's method, Down (*ibid.*, **224**, 195) recommends the addition of a quantity of lime sufficient to neutralise the acid contained in the liquors, and to cause the precipitation of only a very small portion of iron salts present in the solution. Arsenic and antimony are said to go down with the copper in strongly acid solutions, in weaker solutions they remain dissolved; according to Kingzett and Lunge they are said to form a compound with iron similar to Scheele's green.

2. *Desilvering the Liquors.*—According to Claudet, the liquors are treated with potassium iodide, the moist precipitate is acidified with hydrochloric acid and zinc is added, zinc iodide and silver being formed. Owing to the high price of iodine varec liquors are now used.

Gibb desilvers by partial precipitation with hydrogen sulphide obtained from the residues of alkali works. The greater portion of the silver is thrown down with the first 6 per cent. of copper sulphide precipitated. Sodium sulphide is also used.

Snelus precipitates about 19 per cent. of the copper from the liquors of burnt ores, by blowing finely divided iron dust into the liquors and agitating the mixture, whereby 80 per cent. of the soluble silver is thrown down.

Chadwick and Jardine precipitate with lead acetate, remove the copper in the precipitate by treatment with hot dilute sulphuric acid, and reduce with zinc and sulphuric acid.

Clark and Smith treat the chlorinated ores with cold water, then with a solution of sodium thiosulphate or with gas-liquor, in order to obtain silver chloride in solution, from which the metal is separated by galvanic means. The residual liquor is mixed with that yielded by the extract of the ore in hot water, to separate the copper.

IV. *Precipitating the Copper.*—Iron is mostly used for separating the copper from the liquors, wrought-iron being more active than cast-iron. Spongy iron is the best. The apparatus used consists of large boxes provided with steam pipes and agitators.

Hydrogen sulphide is used by Wagner for precipitating the hydrochloric acid extract. The gas is obtained from barium sulphide and hydrochloric acid. The hydrochloric acid used for extracting the copper is recovered in the liquid from which the sulphide has been precipitated.

Krassinsky and Wissocq use lime as precipitant.

V. *Treating the Product and Residues.*—1. *Products.*—The copper obtained by cementation is collected and washed. It is either sold in this form or worked up into a purer product.

The copper sulphide obtained by precipitation with sulphuretted hydrogen or alkaline sulphides is washed and worked up into coarse metals.

Copper sulphate is obtained in the desilvering operation. The product forms a commercial article.

Oxides of copper are worked up into black copper.

The extracted residue (purple ore) consists essentially of ferric oxide (95 per cent.). It is free from sulphur and is used for lining puddling furnaces, or it may be melted in the blast furnace.

2. *Condensation of the Roasting Gases.*—In chlorinating, according to Henderson's method, a small quantity of copper is carried off with the gases evolved. These are condensed in towers, so that the copper is recovered as well as the hydrochloric and sulphuric acids.

3. *Residual Liquors.—Partial Recovery of the Solvents.*—H. Wagner proposes to recover the acid used for dissolving the iron in the ores, by exposing the neutral residual liquors to atmospheric oxidation with constant agitation. Basic salts of iron are deposited and the acid in the solution liberated.

The bye-product obtained in conjunction with the recovery of the solvents is iron sulphate obtained from those liquors, which remain on extracting the ores after sulphuration: it always contains aluminic sulphate. Baryta preparations are obtained in Wagner's process. Glauber salt is obtained from the final liquors in Henderson's method. Iron oxide is recovered in the form of a red pigment, sodium sulphide, and soda.

Electrolysis used in the Copper Metallurgy.—In 1835—1840 Becquerel made a number of trials with a view of obtaining silver, copper, and lead from their ores by electro-chemical means. The ores were in the first place chlorinated and sulphurated. Chains were then introduced into the clear liquid. These consisted of zinc, iron, or lead, in combination with copper. The plates of the non-oxidisable metals were brought into direct contact with the silver solution, whereas the oxidisable metal was placed in porous diaphragms of canvas, which were filled with salt water and put into the solution containing the ore. They were then connected metallically with the former.

In 1867 Patera published a method of extracting copper from cement water, which consists in filling cells of clay or fir-wood with iron plates and connecting the latter with the cathode, consisting of small pieces of coke, a moderately strong solution of salt being used to produce the action.

Keith's method of preparing copper electrolytically is well known.

D. B.

Fire-damp in Collieries. By C. Winkler (*Dingl. polyt. J.*, **231**, 280—282).—The author describes in *Jahrbuch für das Berg-und Hüttenwesen Sachsens*, 1878, various apparatus for indicating fire-damp in coal mines. Schöpfleuthner uses a scale, a glass flask filled with air being fixed to one end of the beam. The scale is in equilibrium in normal air, but when the latter is mixed with lighter or heavier gases the flask sinks or rises, and the opposite end of the beam is brought into contact with an electric current, which it closes, and thus causes the sounding of an alarm bell.

It is mentioned that the difficulty of obtaining fair samples of the air in mines has been the only reason that chemical investigations in this direction have failed to give trustworthy results. Besides this, other circumstances, *e.g.*, changes of weather, alterations in temperature, and pressure often effect the liberation of fire-damp, and thus further depreciate the value of chemical investigation. However, it is stated by the author that it cannot be foretold what problems as to the consistency, formation, accumulation, and removal of choke- and fire-damp may be solved, by adding to the usual observations of deter-

mining the conditions of ventilation, temperature, and pressure, analyses of the air in mines. In the Epinac collieries of Montceau-les-Mines these analyses are made constantly, "grisometers" being fixed at various parts of the pit, and the amount of marsh-gas present in the air noted four times during every shift. D. B.

Absorbing Power of Wood-charcoal. By Jaillard (*Chem. Centr.* [3], 1879, 13).—Wood-charcoal, if sprinkled with water and exposed to the air for three days, was found to undergo the same percentage loss of weight by exposure to 110° for two hours as another sample which had not been wetted. Further, charcoals prepared from different kinds of wood, if exposed for a sufficient length of time to the same atmosphere, lost when heated to 110° for two hours percentages varying between 9 and 10, the humidity of the atmosphere having been 80 per cent. Hence the author concludes that different kinds of wood-charcoal have nearly identical absorption coefficients for moisture. The quantity of moisture absorbed varies, however, with the humidity of the atmosphere. F. C.

Process for Bleaching Vegetable Fabrics. By C. Beyrich (*Chem. Centr.* [3], 1878, 815—816).—In the ordinary process, it is necessary before employing the bleach to remove the gummy materials from the fibre by long-continued boiling with soda. This weakens the fibre, and exposes it more fully to the rotting action of the bleach. The author of the new process uses oxalic acid or potassium oxalate instead of a mineral acid for acting on the bleaching powder. He finds that the preliminary treatment with soda can then be dispensed with, and that the bleaching powder has a greater bleaching effect, and acts less injuriously on the fabric. The author believes that hypochlorous acid is set free, and being decomposed in contact with the fabric, the nascent chlorine and oxygen so produced exert the powerful bleaching effect. A portion of the oxalic acid may also dissolve away the gummy matters and cleanse the fibre. The bleaching powder is mixed with only a portion of the requisite quantity of oxalic acid at first, then the articles are quickly introduced, and the rest of the acid added after a time. The temperature of the bath should be 18—20° C., or at the highest 25—28°. On removal from the bath, the material is freed from the liquid and treated with a dilute sulphuric acid bath to convert all calcium salts into sulphates, and finally the acid is removed by a weak soda-bath. These processes are repeated if necessary, and finally the materials are exposed to sunshine. Only those fabrics which refuse to be wetted by water require to be treated first with soda. F. C.

Composition of "Grains" from Malt. By A. Hilger (*Landw. Versuchs.-Stat.*, **23**, 455).—The following are the results of the author's analysis of malt grains (mash refuse); (A) of dark-coloured grains from a high dried malt; (B) of a lighter variety:—

	Ash, per cent.	Fat, per cent.	Proteïds, per cent.	Sugar, per cent.
A	2·07	4·57	5·75	4·95
B	1·91	5·64	6·02	6·3

The sugar represents, in addition to that present as such, the starch, dextrin, &c., of the grains, which were converted into sugar by the action of dilute sulphuric acid at 100°. C. F. C.

The Amount of Sulphuric Acid in Wines. By G. Lunge (*Deut. Chem. Ges. Ber.*, **12**, 928—930).—The author points out that Nessler's statement (*Zeits. Anal. Chem.*, **18**, 236) that pure wine may contain as much as 3·28 grams of sulphuric acid or 5·83 grams of potassium sulphate is erroneous, and that it is based on the misprint *centi-* for *milli-grams* in Martz's article (*Jour. Pharm. Chim.*, 1877, 273).

W. C. W.

Plastering of Wine. By G. Pollacci (*Gazzetta chimica italiana*, **9**, 37—47).—In a former communication (*Gaz.*, **8**, 379, and this vol., p. 681), the author described the effect produced by adding plaster to wine which had already been fermented: if, however, it is added to the must and fermented with it, very different results are obtained, one of the most noticeable being the great increase in the amount of hydrogen potassium sulphate remaining dissolved in the wine. If the wine itself is plastered, there is only about 1 gram of this salt present per litre, but if the plaster is fermented with the must, it may amount to as much as 5—6 grams per litre. The cause of this difference is the comparative insolubility of the hydrogen potassium tartrate in dilute alcohol; fermented wine of 11 per cent. alcohol cannot retain in solution more than 2—2·2 grams per litre of the tartrate, whilst the grapes from which the litre of wine is made may contain 10—11 grams or even more, and this tartrate, reacting with the calcium sulphate, gives in the first case about 1 gram, and in the second 5—6 grams of hydrogen potassium sulphate, together with the corresponding quantity of calcium tartrate. Besides the sulphate of potash, the wine, whether plastered during fermentation or afterwards, contains much calcium tartrate and sulphate, so that generally speaking, it may be regarded as a saturated solution of these calcium salts. The author finds, moreover, that during the fermentation, the calcium sulphate undergoes reduction, and hydrogen sulphide is evolved; this is also the case with grapes which have been sulphured if any of the sulphur is left adhering to them, and that even when no calcium sulphate is present: this hydrogen sulphide then reacts with the alcohol, giving rise to mercaptan, which greatly damages or entirely spoils the flavour of the wine, the effect being proportional to the amount of plaster added, and the time occupied by the fermentation. If a few drops of the wine thus injured be poured on the palm of the hand and allowed to evaporate, the characteristic odour of mercaptan can be easily recognised. The fermentation of plastered must commences briskly, but gradually diminishes, proceeding more slowly than that of unplastered must; moreover, it is completed with greater difficulty. Wines made from plastered must therefore always contain more glucose and less alcohol than those made from unplastered must. The chief cause of the incomplete fermentation appears to be the hydrogen sulphide, for by direct experiment the author has found that although the presence of a minute quantity of hydrogen sulphide does not interfere with the fermentation, a somewhat larger proportion retards it, whilst a large

quantity entirely prevents fermentation from commencing. An analysis of a wine made from a must which had been fermented with plaster gave the following per litre: calcium sulphate, 1·300 gram; hydrogen potassium tartrate 0·252; and hydrogen potassium sulphate 4·822.

C. E. G.

Changes which Wine undergoes when kept. By BERTHELOT (*J. Pharm.* [4], **29**, 489—493).—Two specimens of port wine were examined, one of which had been kept since 1780, nearly 100 years, and the other 45 years. The wine 100 years old had a clear yellow colour; the colour of the other was darker, but it was not so highly coloured as new port. The taste of the old wine was dry and slightly bitter; there was a large deposit of colouring matter. The older wine had the sp. gr. ·988 at 10°, and the other the sp. gr. 0·991 at 10°.

The results of the analysis are as follows :—

	Port wine 100 years old. Per cent.	Port wine 45 years old. Per cent.
Residue dried at 100°	3·36	5·50
Sugars (reducing)	1·25	3·15
,, after action of dilute acid	1·29	3·68
Acid (calculated as tartaric acid)	5·17	5·46
Tartaric ether (calculated as tartaric acid)	1·11	1·17
Cream of tartar	0·27	0·42

The small quantity of residue in the old wine is perhaps due to the decomposition of the sugar: the residue of new port varies from 3·75 to 5·24; the bases contained in it are potash, lime, and a trace of iron.

The quantity of cane-sugar in the older wine is practically nil, whereas the quantity contained in the other amounts to 0·53 per cent. These results confirm those of the author relative to the slow invertive action of organic acids on cane sugar.

The quantities of ethyltartaric acid corresponding with the acid, existing as such, are respectively 2·66 and 2·83. The total quantity of free tartaric acid in each case corresponds with that contained in new wine, therefore by keeping the wine, it loses about a quarter of its acidity by etherification.

The analyses of the deposits give the following results :—

	Wine 100 years.	Wine 45 years.
Sugar (reducing)	1·25	3·15
Cane-sugar	0·04 (?)	0·53
Pure acids	0·51	0·52
Acids (as ethers)	0·27	0·28
Cream of tartar	0·03	0·04
	2·10	4·52
Glycerin	1·16	0·98

The quantities of alcohol contained in the wine are—

Wine 100 years old, 19·8 per cent. by vol.; 15·9 per cent. by weight.

Wine 45 years old, 20·1 per cent. by vol.; 16·1 per cent. by weight.

The quantities agree with that contained in new wine, which varies from 19 to 23 per cent. by vol.

The gas extracted from the wine 45 years old consisted of nitrogen and oxygen only, 1 litre yielding 44·7 c.c., of which 12·4 c.c. was oxygen and 32·3 nitrogen. It may be remarked that whilst port wine contains oxygen, there is not a trace in Burgundy, which on the other hand contains carbonic anhydride. This gas, however, disappears in old port.

The difference in the constitution in the two port wines is due to the action of the absorbed oxygen on the older. L. T. O'S.

A Critical Point in making Parmesan Cheese. By A. Galmiberti (*Landw. Versuchs.-Stat.*, **23**, 437—442).—Owing to the peculiar manner in which Parmesan cheese is manufactured, there are several critical points in the process which give the maker some trouble. When the curdled milk is sweet and of the usual character, failure generally arises from presence of too much whey in the cheese. If the cheese has not been sufficiently purified by boiling, or has been brought directly into a warm medium before the action of the salt (the withdrawal of serum) has had time for completion, the ferments contained in the cheese begin to act; carbonic anhydride is evolved, which gives rise to bubbles in the cheese paste; and a continuous decomposition sets in, by which the cheese is entirely poilt.

In addition to the above causes of failure there is another which is not so easily recognised. The phenomena of the coagulation of milk and blood are essentially similar: and it is a well-known fact that if blood be shaken during coagulation, the corpuscles do not all combine with the fibrin to produce the clot, but remain partly suspended in the serum. An analogous phenomenon occurs in the preparation of cheese, and if the agitation of the curdling mass has been too violent, a large quantity of the fat globules will pass into the whey, and the cheese will be consequently poorer.

In order to give an idea of the amount of fat which passes into the whey, the author has performed several analyses, from which he draws the following conclusions:—Whey is always more acid and of less specific gravity than milk, and contains about half the amount of solids, with one-eighth the quantity of fat which is present in milk. If therefore 400 litres of milk per diem were used in making cheese, 700 kilos. of fat would pass into the whey in one year. J. K. C.

General and Physical Chemistry.

Continuous Spectrum of the Electric Spark. By A. Abt (*Ann. Phys. Chem.* [2], **7**, 159—160).—If an electric spark is passed through a liquid, instead of a gas, a bright continuous spectrum is obtained in place of a line spectrum. This spectrum, in the case of water and of olive oil, is characterised by its large number of blue rays, and its want of dark red rays. With other liquids, as bitter-almond oil, glycerol, alcohol, and milk, differences in the dispersion of the entire spectrum and of the single colours are obtained, as well as in the intensity of the latter. The most probable explanation of this phenomenon is that the particles separated from the copper electrodes become of a white-hot redness, even in presence of water or another liquid, whilst the constituents of the air do not become so heated. Hence the spectrum loses the line character, and the continuous spectrum of the white-hot metallic particles is all that is visible. T. C.

Boiling Points of Normal Ethanes (Paraffins). By M. Goldstein (*Deut. Chem. Ges. Ber.*, **12**, 689—692).—On comparing the differences between the boiling points of a series differing by CH_2, it is found that these differences become less as the molecular weight increases, *e.g.*, the difference between the boiling points of C_4H_{10} and C_5H_{12} is 38°, whilst that between C_7H_{16} and C_8H_{18} is 25°, so that some other factor must be involved besides the increase of molecular weight. This factor the author considers to be the proportion of hydrogen atoms to carbon atoms in the molecule. The proportion in the ethanes is $2 + \frac{2}{n}$: if numbers are substituted for n, a table can be constructed, of which the following are examples:—

		Differences.
If $n = 1$, the formula gives	4·00	—
$n = 2$ „	3·00	1·00
$n = 3$ „	2·66	0·33
$n = 4$ „	2·50	0·166 &c.

Hence it appears that increase of molecular weight is attended with a decrease of the differences in the boiling points, as well as a decrease in the proportion of hydrogen to carbon-atoms. The difference between the boiling points of two neighbouring ethanes approaches 19 more nearly as the molecular weight increases, but never exactly reaches it (where it does so apparently, the ethanes are not pure). In this way any ethane must boil at $19 + \alpha°$ higher than its next lower homologue. Since the difference between the proportion of hydrogen-atoms to carbon-atoms between two neighbouring homologues is $2 + \frac{2}{n} - \left(2 + \frac{2}{n+1}\right) = \frac{2}{n(n+1)}$, it follows that $\alpha = \int\left(\frac{2}{n(n+1)}\right)$.

A further examination of this question has shown that the assumption of a direct proportionality between the variations of the magnitudes α and $\frac{2}{n(n+1)}$ leads to so close an agreement between the observed and calculated boiling points, that the actual existence of this proportionality may be safely assumed as the basis of further calculation. Denoting, therefore, by α' the function of a new difference, $\frac{2}{n'(n'+1)}$, we shall have $\frac{\alpha}{\alpha'} = \frac{\frac{2}{n(n+1)}}{\frac{2}{n'(n'+1)}}$, and $\alpha' = \frac{n(n+1)}{n'(n'+1)}\alpha$.

In this way it is possible to determine either of the values α', if the value of α which corresponds with a certain difference $\frac{2}{n(n+1)}$ is known. For example, if $n = 4$, α' may be found as follows:—The difference between the boiling points of two neighbouring hydrocarbons is $19 + \alpha$: as C_4H_{10} boils at 1° and C_5H_{12} at 3·9°, the difference is $38 = 19 + \alpha$, hence $\alpha = 19$. If in the above equation we put 19 instead of α and 4 instead of n, we shall have—

see under p. 1168 [$\alpha' = \frac{4(4+1)}{n'(n'+1)} \times 19 = \frac{380}{n'(n'+1)}$.]

The value of α' varies with that of n': but if α' is known for any ethane, the difference $(19 + \alpha')$ between its boiling point and that of the following homologue is easily found. To determine this put $\frac{380}{n'(n'+1)}$ in place of α', and the equation becomes $19 + \alpha' = \frac{380}{n'(n'+1)} + 19$.

A table constructed from this formula shows that the calculated and observed boiling points approximate closely. G. T. A.

Vapour-density Determinations of Inorganic Bodies at High Temperatures. By V. and C. Meyer (*Deut. Chem. Ges. Ber.*, **12**, 1112—1118).—For temperatures above a red heat the following modifications of the author's process (*Ber.*, **12**, 609) must be employed. The substance is contained in a small cup made from the stem of a Dutch clay pipe. The vessel in which the determination is carried on is made of glazed porcelain. It is first cautiously heated in an ordinary muffle furnace, and then transferred to a muffle heated by a Perrot's gas furnace. Before introducing the substance, the air in the apparatus is displaced by a current of nitrogen. If care is taken to ensure the gradual cooling down of the furnace, the same porcelain vessel may be employed for several determinations.

The following numbers were obtained:—

	Found.	Calculated.
Sulphur above a red heat (S_2)	2·17	2·21
Cu_2Cl_2	7·05	6·84
As_4O_6	13·78	13·68
Cinnabar (is resolved into S and Hg)	5·39	—

W. C. W.

Heat of Formation of Cyanogen. By Berthelot (*Compt. rend.*, **88**, 877—879).—By direct experiments the author finds that the heat liberated by the combustion of 26 grams of cyanogen in oxygen is, all corrections being made, 132·3 cal. This exceeds by 38·3 cal. the heat of combustion of the contained carbon referred to the state of diamond, and the difference represents the heat absorbed in the formation of cyanogen from its elements. This number differs but little from that otherwise deduced by the author, when in 1864 he first pointed out the absorption of heat attending the formation of cyanogen. Cyanogen, acetylene, and NO_2, all well defined compound radicles, are formed from their elements with absorption of heat; and this circumstance is probably connected with their energy of combination, which is so much greater than that of their constituent elements in the free state. R. R.

Thermic Formation of Silicon Hydride. By J. Ogier (*Compt. rend.*, **88**, 911).—The gas was prepared by decomposing silicoformic ether with sodium, so as to obtain it free from hydrogen. The heat of combustion in oxygen of one equivalent in grams of SiH_4 was found by direct experiment to be 324·3 cal., which is less by 24·8 than the heat of combustion of the constituents. The union of Si and H_4 is therefore accompanied by a disengagement of heat = 24·8 cal. This number is nearly the same as that representing the heat of combination of the constituents in marsh-gas (22 cal.), and SiH_4 is also decomposed by electric sparks with deposition of amorphous silicon. R. R.

Thermic Researches on Silicic Ether. By J. Ogier (*Compt. rend.*, **88**, 970—972).—By two methods—one synthetic, the other analytic—the author has determined the heat of formation of silicic ether from pure alcohol, and of silicic alcohol dissolved in water. The results agree closely, and their mean value is 11·5 cal. for the equivalent in grams. The author also finds the specific heat of silicium chloride between 13° and 15° to be 33·9 cal., and its heat of vaporisation at the atmospheric pressure 6·3 cal. The specific heat between 15—84°, and the heat of vaporisation of silicic ether, are 88·7 and 7 cal. respectively. R. R.

Influence of Substitution on Evolution of Heat during the Formation of Salts. By W. Louguinine (*Deut. Chem. Ges. Ber.*, **12**, 696).—Aniline and paratoluidine are much weaker bases than ammonia. Aniline evolves 7·44 heat units on combining with hydrochloric acid. The introduction of chlorine into the aniline molecule lessens the amount of heat set free during combination with hydrochloric acid.

Paranitraniline evolves considerably less heat on combination with hydrochloric acid than chloraniline does. More heat is evolved by the action of monochlor- and trichlor-acetic acid on Na_2O than by acetic acid, and monochloracetic acid evolves more than trichloracetic acid. Amidacetic acid combines with Na_2O and hydrochloric acid without any considerable evolution of heat.

Alanine behaves similarly. Nitrobenzoic acid evolves more heat than benzoic acid if the compounds are regarded as reacting in the absence of water: in solution the influence of the nitro-group is scarcely noticeable. Similarly in the case of trichloracetic acid, although it evolves more heat in solution than acetic acid does, the difference is considerably greater if the bodies are considered apart from the water. The introduction of the group NH_2 into the molecule of benzoic acid considerably lowers the heat evolved on combination with Na_2O, but not to the same extent as in the fatty acid series. Amidobenzoic acid evolves 275 heat-units on combination with hydrochloric acid. The introduction of the nitro-group into the phenol-molecule increases the heat evolved by the action of Na_2O in proportion to the number of substitutions. In this respect the introduction of NO_2 has the same effect as that of two atoms of chlorine. The nitro-group behaves similarly in aniline and its homologues. Finally, the heat evolved by the action of the three isomeric nitrophenols on Na_2O is nearly but not quite the same for all. The three isomeric monochloranilines show a similar behaviour. G. T. A.

Volume-constitution of the Sulphates, Selenates, and Chromates of the Magnesium Metals. By H. Schröder (*J. pr. Chem.* [2], **19**, 266—294).—The author's method of calculating the so-called molecular volume of solid compounds, and of deducing therefrom the *stere* of the constituent elements, has been already explained (see this Journal, 1878, Abs., 926). The stere of Mg, Zn, Fe, Co, Ni, Cu, and Mn, was formerly found to be 5·52.

The following are the most important general conclusions in the present paper. The volumes of the double selenates,—

$$M_2SeO_4.RSeO_4.6H_2O, \text{ and } 2H_2O,$$

are equal to the sum of the volumes of the constituent salts (M = K or NH_4; R = Fe, Co, Ni, Cu, Mn, Zn, or Mg.). The same generalisation holds good for the double sulphates, $M_2SO_4.RSO_4.6H_2O$, and $4H_2O$; and for the double chromates, $M_2CrO_4.RCrO_4.2H_2O$. These double salts are therefore to be regarded as molecular compounds only.

The volumes of the hydrated sulphates, selenates, and chromates of Mg, Zn, Fe, Co, Ni, and Mn are multiples of 5·52, the stere of those metals.

The volume of selenates and chromates is always one stere greater than that of corresponding sulphates.

The volume of the manganese compound is one stere greater than that of the corresponding compound of Mg, Zn, Fe, Co, or Cu; except in the sulphates $MnSO_4.5H_2O$ and $6H_2O$, which are isosteric with the corresponding salts, $RSeO_4.5H_2O$ and $6H_2O$ respectively.

The volume of nickel compounds is one half stere, or sometimes

one stere smaller than that of the corresponding compounds of Mg, Zn, Fe, Co, and Cu.

In the sulphates with 4 mols. of water, the second mol. of water has the volume $H_4^1O_2^2$: in the sulphates and selenates with 6 mols. of water, the second and third mols. of water have the volume $H_4^1O_2^2$.

The following groups of compounds are isosteric:—

$MnSO_4.6H_2O$ and $RSeO_4.6H_2O$, where R = Fe, Co, Cu, Mg, or Zn.
$MnSO_4.5H_2O$ and $RSeO_4.5H_2O$, where R = Cu, Mg, or Zn.

The corresponding chromates and selenates—

$RSO_4.7H_2O$, where R = Fe, Mg, or Zn.
$RSeO_4.5H_2O$, where R = Co, Cu, or Zn; the isomorphous $MnSeO_4.5H_2O$ is not isosteric.
$K_2RS_2O_8.6H_2O$, where R = Co, Cu, Fe, Mg, or Zn.
$(NH_4)_2RS_2O_8.6H_2O$, where R = Co, Cu, Fe, Mg, or Zn.
$K_2RSe_2O_8.6H_2O$, where R = Co, Cu, Mg, or Zn.
$(NH_4)_2RSe_2O_8.6H_2O$, where R = Co or Cu.

The *probable* volume constitution of the sulphates, selenates, and chromates with 2, 4, 5, 6, and 7 mols. of water is discussed in considerable detail in the original paper: the general result is that the volumes of these salts are largely influenced by the degree of condensation of the attached water, and that the amount of this condensation varies in the different mols. of water.

The results obtained with sulphates, chromates, and selenates, after partial and complete dehydration, are very vague and incomplete. The author believes that in many cases they point to the possibility of changes occurring in the steres of the dominating elements, and to the existence of the same compound with different steric values.

M. M. P. M.

Determination of Atomic Weights and the Use of Isomorphism for the Same. By H. Kopp (*Deut. Chem. Ges. Ber.*, **12**, 868—924).—The greater part of this paper consists of a review of the principal methods for determining atomic weights, and especially as regards the assistance rendered by isomorphism. Those substances only should be considered as isomorphous which are capable of forming mixed crystals or which are capable of forming "overgrowths" (*Ueberwachsen*), *i.e.*, when a crystal of the one is suspended in a solution of the other, the crystal increases in size, owing to the deposition on it of the substance in solution, as when a crystal of common alum is suspended in a solution of chrome alum. The best methods of obtaining such crystals are described. Special reference is made to the sulphates of cadmium, didymium, and yttrium, which are usually considered to be isomorphous, being represented by the following formulæ:—$3CdSO_4 + 8H_2O$; $3DiSO_4 + 8H_2O$; $3YtSO_4 + 8H_2O$(Cd = 112, Di = 97, Yt = 60). The author concludes from a number of recent experiments that these compounds do not crystallise in exactly the same form, nor do the sulphates of cadmium and didymium form mixed crystals or "overgrowths." The sulphate of cadmium is, therefore, not isomorphous with the sulphates of didymium and yttrium. The formulæ of these bodies must now be written $3CdSO_4 + 8H_2O = Cd_3S_3O_{12} + 8H_2O$;

$Di_2S_3O_{12} + 8H_2O$; $Yt_2S_3O_{12} + 8H_2O$ (Cd = 112, Di = 145, Yt = 90). This agrees with Hillebrand's determination of the specific heat of didymium.*

The compounds K_2PtCl_6 and K_2SnCl_6, and likewise calcspar and sodium nitrate, are isomorphous, since overgrowths of these pairs of bodies may be obtained. Unlike G. Rose (*Ber.*, **4**, 105), the author was unable to obtain overgrowths of potassium nitrate on arragonite.

T. C.

Inorganic Chemistry.

Action of Chlorine on Anhydrous Metallic Bromides. By A. Potilitzin (*Deut. Chem. Ges. Ber.*, **12**, 695—697).—Dry chlorine acts on metallic bromides slowly, and in a limited manner, depending on the temperature. The reaction begins at the ordinary temperature; but not instantaneously in the case of potassium, mercury, and silver bromides. Sodium bromide is only sparingly acted on after 24 hours under the same conditions, and the substitution of bromine by chlorine in the bromides of barium and strontium begins at 100°. The presence of the slightest trace of moisture essentially promotes the reaction. The experiments were conducted in sealed tubes with excess of chlorine. Oxygen displaces the haloïds from their compounds, with various degrees of facility. Potassium and sodium bromides, and barium and strontium chlorides, when heated with dry oxygen, lose only traces of the haloïd. Chloride of calcium, and the bromides of calcium, barium, and strontium, more particularly calcium bromide, are acted on more easily. The facility with which oxygen replaces bromine in the metallic bromides of the calcium group is inversely proportional to the atomic weights of the elements of the group. The haloïds are also replaced by oxygen in $CdCl_2$, $PbCl_2$, $CdBr_2$, and $PbBr_2$.

With sodium at 20°, 5·48 per cent. of bromine was substituted by chlorine in 36 hours, and after 120 hours, during which chlorine was taken in equivalent quantities 4·99 per cent. From potassium bromide 8·6 per cent. of bromine was expelled by excess of chlorine in 40 hours, 9·58 per cent. in 48 hours, 10·42 per cent. in 34 days, and by an equivalent quantity of chlorine 8·07 per cent. in 144 hours. Excess of chlorine substituted 75·37 per cent. of bromine in silver bromide in 24 hours. Chlorine acts on anhydrous barium bromide only at about 100°: after $3\frac{1}{2}$ hours at this temperature 6·45 per cent. of bromine was expelled.

G. T. A.

Behaviour of the Nitrogen Acids with Sulphuric Acid. By G. Lunge (*Deut. Chem. Ges. Ber.*, **12**, 1058—1060).—Nitrogen tetroxide is decomposed by sulphuric acid, forming nitric and nitrosylsulphuric acids.

* *Note by Abstractor.*—Also with the position assigned by Mendelejeff (*Liebig's Annalen*, Supplebd. **8**, 133) to Di and Yt in the general classification of the elements, according to which these elements are triads and belong to the same group as Al.

Nitrosylsulphuric acid dissolves in an excess of sulphuric acid, forming a colourless solution, which assumes a red colour when heated, but again becomes colourless on cooling. A yellow solution is obtained when the ratio between the nitrosylsulphuric acid and the solvent passes a certain limit which varies with the strength of the sulphuric acid.

Nitrosylsulphuric acid is only slowly decomposed when its solution in strong sulphuric acid is boiled; but if a dilute acid is used, the decomposition takes place more readily, thus most of the nitrosylsulphuric acid is expelled on boiling sulphuric acid, sp. gr. 1·6.

If the acid is more dilute it will contain free nitrous acid. The nitric acid is not readily expelled by boiling. Nitrous anhydride is partly decomposed by soda into nitric acid and nitric oxide, hence considerable loss occurs when the nitrous fumes are absorbed by this substance.

W. C. W.

Crystals Extracted from Cast Iron by Ether or Petroleum. By J. L. Smith (*Compt. rend.*, **88**, 888—890).—When ether or petroleum is shaken up with about 50 grams of finely divided cast iron, and allowed to evaporate spontaneously, acicular crystals are obtained. These melt when heated in a tube, and at a higher temperature volatilise, leaving a carbonaceous residue. The author has obtained a similar product from meteoric graphite. The chief constituent of these crystals is sulphur, but whether the sulphur exists within the mass of the iron in the free state, or is liberated by the action of the air on the sulphide, is a question not yet decided. R. R.

Action of Organic Solvents on Sulphur and Metallic Sulphides. By Berthelot (*Compt. rend.*, **88**, 890).—The author has studied the action of ether on sulphur and on various sulphides of iron. In every case, on the evaporation of the filtered liquid, crystals of pure sulphur were first deposited, and afterwards a compound containing carbon, hydrogen, and a considerable proportion of combined sulphur. This compound is the result of the chemical action of the sulphur on the solvent, aided by the influence of atmospheric oxygen. The reaction is analogous to that which occurs between free oxygen and hydrocarbons, alcohols, ethers, or aldehydes, by which various ill-defined resinous compounds are produced. In the case of iron sulphides treated with ether, the oxygen of the air unites with the metal, setting free the sulphur, which simultaneously acts on the organic solvent. The substance which Lawrence Smith obtained from cast-iron was probably formed in this way, from a trace of sulphide contained in metal. It is evident, therefore, that the so-called neutral solvents do sometimes act chemically on the substances with which they are placed in contact. Hence the pre-existence in meteorites of crystallisable hydrocarbons capable of extraction by organic solvents must be received with great reserve. R. R.

Action of Selenium on Metallic Sulphides. By A. Potilitzin (*Deut. Chem. Ges. Ber.*, **12**, 697).—By the action of equivalent quantities of selenium on the sulphides of copper, silver, and lead at 600—700°, the following results were obtained:—From Ag_2S 66·21, 68·80,

and 68·66 per cent. of sulphur was expelled: from Cu_2S 48·01 per cent.: from PbS 65·72 and 55·51 per cent. The influence of the atomic weights was shown in the few experiments made.

G. T. A.

Behaviour of Silicates containing Fluorine, especially Topaz and Mica, at High Temperatures. By C. Rammelsberg (*Ann. Phys. Chem.* [2], **7**, 146—157).—Some silicates, on fusion, do not undergo any chemical change, as they do not contain any volatile constituents, and some of these even reassume their crystalline form on solidification, but the greater number form a glass, the specific gravity of which is less than that of the original mineral, and which is easily decomposed by acids. There is also a very important class of silicates, which on fusion undergo chemical change, as topaz, mica, tourmaline, &c., owing to the volatilisation of some of their constituents, as hydrogen and fluorine.

Experiments made with various kinds of topaz and mica show that only the former lose the whole of their fluorine at the temperature of a porcelain-furnace, and that too only under favourable circumstances. One part of the fluorine is evolved as hydrofluoric acid, and the rest as the fluosilicate contained in the original mineral, whilst the metals K, Li, Mg, Fe, Al, and Si, existing as fluorides, remain behind as oxides. This confirms the author's view that the fluorine in these silicates is combined in a manner similar to the oxygen. The opinion that the fluorine goes off only as silicon fluoride is therefore incorrect. In the topazes, not only the silicon of the aluminium silico-fluoride, but also a portion of the silicon from the oxysilicates, is converted by the hydrofluoric acid into silicon fluoride and evolved as such. T. C.

Mercuric Iodide. By K. Kraut (*Deut. Chem. Ges. Ber.*, **12**, 1076).—A reply to Köhler's observations on the melting point of mercuric iodide (*Ber.*, **12**, 608). W. C. W.

Atomic Weight of Antimony. By F. Kessler (*Deut. Chem. Ges. Ber.*, **12**, 1044—1047).—The atomic weight of antimony is 122, as determined by Dumas (*Ann. Chim. Phys.* [iii], **55**, 175), Dexter (*Pogg. Ann.*, **100**, 563—578), and the author (*ibid.*, **95**, 204—225, and **113**, 134—155). On the other hand, Schneider (*ibid.*, **98**, 293—305), and more recently Cooke (*Proc. Amer. Acad. of Arts and Sciences*, **13**, 1—71), have fixed the atomic weight of antimony at 120. The author asserts that this latter result is due to the impurities contained in the native sulphide of antimony used in Schneider's experiments, and to the errors which are inherent in Cooke's method of analysis. W. C. W.

Preparation of Iridio-platinum. By G. Matthey (*Chem. News*, **39**, 175—177).—The author describes the methods followed by him in the preparation of an alloy suitable for the manufacture of the international meter and kilogram standards and the geodesic rule.

Preparation of Pure Platinum.—Ordinary commercial platinum is melted with six times its weight of pure lead, and the alloy, after granulation, is treated with successive quantities of dilute nitric acid

(1 to 8), until there is no more action; and the solution, which contains lead, iron, copper, palladium, and rhodium, is separated from the residue and treated by appropriate methods. The residue, an amorphous powder containing platinum, lead, crystalline iridium, and small proportions of other metals, is treated with weak aqua regia, which dissolves the platinum and lead, leaving the whole of the iridium in an impure state. The solution is evaporated, the lead removed by sulphuric acid, the platinum solution is again evaporated, and the platinum chloride dissolved in water and mixed with an excess of ammonium and sodium chlorides. The solution, kept at 80° for several days, deposits the ammonio-chloride of platinum, which is removed, and after being washed with saturated ammonium chloride and then with hydrochloric acid, is dried; and as it may still contain rhodium, it is mixed with potassium-hydrogen sulphate and a little ammonium-hydrogen sulphate, and gradually heated to dull redness in a platinum capsule. The platinum is reduced in the form of a black powder, the rhodium remaining as rhodium and potassium bisulphate, which is completely dissolved out by digestion with boiling water; the solution contains also a little platinum, which is recovered by evaporating to dryness and heating the residue to redness, at which temperature the platinum salt alone is decomposed. The absolutely pure platinum obtained by this process has a density of 21·46.

Preparation of Pure Iridium.—The iridium obtained from an ordinary solution of this metal (freed from osmium by long boiling in aqua regia), by precipitation with ammonium chloride, contains traces of platinum, rhodium, ruthenium, and iron; the presence of platinum is unimportant when iridio-platinum is to be prepared. This iridium is fused for some hours with ten times its weight of lead; the lead dissolved out from the alloy by nitric acid; the residue subjected to a prolonged digestion with aqua regia; and the crystalline mass which remains is then fused at a high temperature with potassium bisulphate in order to remove rhodium. The partially purified iridium is next melted for some time with 10 parts of dry potassium hydrate and 3 of nitre in a gold crucible. The mass treated with cold water furnishes a solution containing potassium rutheniate and a "blue residue" of potassium iridiate, which is washed with water containing potassium hydrate and sodium hypochlorite until the washings are colourless; then with distilled water; and then mixed with a solution of sodium hypochlorite and allowed to stand for some time. The mixture is next transferred to a retort, warmed, and finally boiled until the distillate no longer imparts a red colour to weak alcohol acidulated with hydrochloric acid (ruthenium). To remove the last trace of ruthenium from the residue, the treatment with nitre and potash and with sodium hypochlorite is repeated. The blue powder is then dissolved in aqua regia; the solution evaporated to dryness; the residue dissolved in distilled water; and the solution is filtered and poured slowly into concentrated solution of soda containing sodium hypochlorite (no precipitate should be formed), which is then subjected in a distilling apparatus to a current of chlorine, the distillate being tested for ruthenium. The blue oxide of iridium precipitated by the chlorine is collected, washed, dried, and reduced in a glass tube by a current of

the mixed gases (CO + CO_2), obtained by gently heating a mixture of oxalic and sulphuric acids. The metallic iridium is heated to redness with potassium bisulphate to remove unreduced oxide of iron and traces of rhodium, and the insoluble portion, after many washings with water, is washed with chlorine water to remove traces of gold, and with hydrofluoric acid to free it from silica. The remaining iridium, after calcination in a charcoal crucible, is melted to an ingot, which, after being broken up and boiled with hydrochloric acid to remove adhering iron, should, if perfectly pure, be of sp. gr. 22·39. The purest iridium prepared by the author had density 22·38, and still contained almost inappreciable traces of oxygen, rhodium, ruthenium, and possibly iron.

Alloy of Iridio-platinum.—450 ounces of platinum and 55 ounces of iridium were melted together; and the resulting ingot was cut into small pieces by hydraulic machinery, then remelted and forged at a white heat under a steam hammer (the surfaces of which were cleaned and highly polished after each series of blows); passed through polished steel rollers; cut into narrow strips; and again slowly melted in a properly-shaped mould. This ingot, forged into a bar 35 cm. × 7·5 cm. × 2·5 cm., showed at zero a density = 21·522; after a second forging and rolling, the density was 21·648. After the bar had been passed through highly polished rolls until the dimensions were 40·80 cm. × 21 mm. × 5 mm., a perfectly rectangular form was given to it by drawing through a series of plates. The rule thus prepared for polishing had a density = 21·516, and gave on analysis:—

Platinum	89·40	89·42
Iridium	10·16	10·22
Rhodium	0·18	0·16
Ruthenium	0·10	0·10
Iron	0·06	0·06
	99·90	99·96

The density calculated from the first analysis is 21·510, and from the second, 51·515, which coincides with the actual determination.

The rule thus prepared for the *Association Géodésique Internationale* was perfectly free from flaws, susceptible of a splendid polish, and much more suitable than platinum for the dividing process.

Iridio-platinum possesses the following advantages for standard rules and weights:—It is almost indestructible, has extreme rigidity, especially in the tube form, and a most beautifully polished surface can be obtained; its coefficient of elasticity is very great and its density very high. For weights, the alloy should contain not less than 20 per cent. of iridium. Such an alloy, sp. gr. 21·614, has a coefficient of elasticity = 22·2, one of the highest known, whilst its malleability and ductility are almost without limit. The kilogram prepared from it measures only 46·266 c.c., displacing 2·267 c.c. less than the kilogram of the archives of France. Alloys containing more than 20 per cent. of iridium are very difficult to work.

J. M. H. M.

Organic Chemistry.

On Copper and Ammonium Oxyferrocyanide. By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 435, 436).—By adding potassium ferrocyanide to ammoniacal copper sulphate, an ochreous precipitate of copper ammonium ferrocyanide is formed. When dried and heated to 150—170°, this body loses a certain proportion of ammonia and cyanogen, and absorbs oxygen, whilst its colour changes to violet. It consists of a copper-ammonium oxyferrocyanide; it is not acted on by air or light, but cannot be used as a pigment.

On heating this violet compound to 200°, it loses ammonia and cyanogen, without absorbing oxygen; and its colour changes to a deep blue, which is as stable as the violet, the change being due to the formation of a more highly oxidised compound.

The blue compound is still further oxidised by heating it to 240—250°, when it loses more ammonia and cyanogen, and assumes a dark green colour. At 300° this compound is completely decomposed, leaving a residue of copper and ferric oxide. L. T. O'S.

Methyl and Ethyl Sulphates. By P. Claesson (*J. pr. Chem.* [2], **19**, 231—265).—The method adopted for the preparation of methyl and ethyl sulphates by the author is that employed by Baumstark (*Annalen*, **140**, 78) and by Orlowsky (*Ber.*, **8**, 332; this Journal, 1875, 875): viz., the action of sulphuric monochloride on methyl or ethyl alcohol. The results obtained do not, however, corroborate those of the two chemists cited. According to Baumstark, sulphuric monochloride acts violently on ethyl alcohol, with separation of carbon and production of ethyl sulphate and ethyl-hydrogen sulphate. The author concludes from his own experiments that Baumstark's sulphuric monochloride really consisted of pyrosulphuric chloride containing considerable quantities of phosphorous chloride, or perhaps phosphorus oxychloride. In addition to the work of Orlowsky already referred to, a paper was published by Mazurowska (*J. pr. Chem.* [2], **13**, 158; this Journal, 1876 [2], **61**). These papers are severely criticised by the author; he believes them to have been written by the same chemist. According to Orlowsky-Mazurowska, the action of sulphuric monochloride on ethyl alcohol may be thus formulated: $2EtOH + SO_2(OH)Cl = Et_2SO_4 + HCl + H_2O$. The normal ethyl sulphate is decomposed by water, according to the same authority: hence in this reaction a portion of the normal sulphate must have been decomposed. The properties ascribed by Orlowsky-Mazurowska to ethyl sulphate are not characteristic of that substance when pure; the compound examined by him probably contained sulphuric, phosphoric, and hydrochloric acid, and methyl chlorosulphonate. If pure methylic alcohol be allowed to drop slowly into sulphuric monochloride surrounded by ice, an energetic action takes place, with production of methyl-hydrogen sulphate and hydrochloric acid, thus: $SO_2(OH)Cl + MeOH = MeHSO_4 + HCl$. *No* water is formed during the reaction. If the acid be added to the alcohol, the

same reaction occurs, but a portion of the hydrochloric acid reacts with the alcohol, producing methyl chloride and water, which latter substance again decomposes some of the sulphuric monochloride, with formation of hydrochloric and sulphuric acids. An analogous action occurs when ethyl alcohol is slowly added to sulphuric monochloride, $SO_2(OH)Cl + EtOH = EtHSO_4 + HCl$. If the temperature be allowed to rise during the action, a considerable amount of ethyl chlorosulphonate is produced, $SO_2(OH)Cl + EtOH = SO_2(OEt)Cl + H_2O$. The production of ethyl (or methyl) hydrogen sulphate by the action of concentrated sulphuric acid on ethyl (or methyl) alcohol is well known. The author's experiments confirm those of Berthelot (*Bull. Soc. Chim.* [2], **19**, 295; this Journal, 1873, 869), viz., that when equal mols. of acid and alcohol are employed, from 57 to 59 per cent. of ethyl (or methyl) hydrogen sulphate is obtained. Employment of a greater quantity of either acid or alcohol increases the yield of acid salt; the maximum amount (77 per cent.) is obtained by using 3 mols. alcohol to 1 mol. sulphuric acid.

Pure methyl-hydrogen sulphate is an oily liquid, which does not solidify at $-30°$; it is soluble in absolute ether. When it is diluted with water, much heat is evolved, pointing to the formation of definite hydrates, but none of these could be obtained in the form of crystals, as stated by Dumas and Peligot (*Ann. Chim. Phys.*, **58**, 54); it seems also to form molecular compounds with methyl alcohol. When methyl-hydrogen sulphate is heated to 130—140° in a vacuum, it is decomposed in accordance with the equation $2MeHSO_4 = Me_2SO_4 + H_2SO_4$. Methyl sulphate has been described by Dumas and Peligot (*loc. cit.*). Their observations are confirmed by the author; he, however, differs from these chemists as to the odour of this substance. Methyl sulphate undergoes partial decomposition when repeatedly distilled under ordinary atmospheric pressure; when heated to a high temperature with water or methyl alcohol, it is decomposed, with formation of methyl-hydrogen sulphate and methyl alcohol or ether.

The properties of ethyl-hydrogen sulphate are analogous to those of the methyl compound; it is decomposed on distillation, with production of ethyl sulphate and sulphuric acid, but carbon is simultaneously separated, and sulphurous anhydride is evolved.

Ethyl sulphate can also be prepared by the action of ethyl alcohol on ethyl chlorosulphonate (see *post*), and by heating silver sulphate and ethyl iodide with a little alcohol and absolute ether in sealed tubes at 150°. This compound is, however, most easily obtained by mixing absolute alcohol (surrounded by ice) and sulphuric acid in molecular proportion, diluting with water, and extracting with chloroform.

Ethyl sulphate is a colourless oily liquid, of pleasant odour; it boils at 208° under ordinary atmospheric pressure, with slight decomposition; it may be distilled unchanged in a vacuum; sp. gr. at $19° = 1·1837$. Ethyl sulphate is insoluble in water, but is very slowly decomposed thereby, with production of ethyl-hydrogen sulphate and ethyl alcohol. In the presence of much water and at high temperatures, this decomposition proceeds more rapidly.

The so-called ethyl sulphate obtained by Wetherill (*Annalen*, **66**,

117) by the action of gaseous sulphuric anhydride on ether or alcohol has been examined by the author, who confirms Erlenmeyer's result (*Annalen*, **162**, 382), that this oil is a mixture of ethyl sulphate and ethyl isethionate (ethyl ethoxysulphonate), $EtO.SO_3Et$. If absolute ether, free from alcohol, be employed in Wetherill's process, the main product of the action is ethyl sulphate.

It has been already mentioned that ethyl sulphate may be prepared by the action of ethyl alcohol on ethyl chlorosulphonate. The mutual action of these bodies is very energetic; it may be represented by the following equations:—

(1.) $SO_2(OEt)Cl + EtOH = EtCl + EtHSO_4$.
(2.) $SO_2(OEt)Cl + 2EtOH = Et_2O + HCl + EtHSO_4$.
(3.) $SO_2(OEt)Cl + EtOH = Et_2SO_4 + HCl$.

It is possible that the ether is produced by a secondary reaction between ethyl sulphate and alcohol: $Et_2SO_4 + EtOH = Et_2O + EtHSO_4$, and not by the direct reaction formulated in (2).

Behrend (*Ber.*, **9**, 1334, this Journal, 1877, **2**, 290) represents the action of ethyl alcohol on methyl chlorosulphonate, or of methyl alcohol on the corresponding ethyl salt, as yielding methyl-ethyl sulphate, $MeEtSO_4$. These results are pronounced by the author to be altogether incorrect.

In preparing ethyl chlorosulphonate by the action of ethylene on sulphuric monochloride, a dark-coloured residue remained in the retort. By dissolving this residue in water, neutralising with barium carbonate, decolorising by filtration through animal charcoal, and precipitating by addition of alcohol, a mass of crystals was obtained, which, on purification and analysis, proved to be *barium ethionate*, $C_2H_4.OSO_3.SO_3Ba$. As isethionic acid is easily prepared from barium ethionate, the action of ethylene on sulphuric monochloride affords a most ready method for the preparation of the former acid. Probably ethionic acid is produced by the action of sulphuric monochloride on previously formed ethyl chlorosulphonate. Thus: $SO_2(OH)Cl + SO_2(OEt)Cl = C_2H_4.SO_3Cl.SO_3H + HCl$. On adding water, the chlorethionic acid is decomposed.

The author has repeated the experiments of Gerhardt (*Traité de Chimie Organique*) on the effect of boiling a solution of barium ethylsulphate, which led that chemist to believe in the existence of *parathionic acid*, an acid isomeric with ethyl-hydrogen sulphate. Gerhardt's barium salt probably contained a little ethyl sulphate, the presence of which would account for the reaction obtained. In the author's opinion, parathionic acid does not exist. M. M. P. M.

Preparation of Nitromannite, and the Conditions of its Explosion. By N. Sokoloff (*Deut. Chem. Ges. Ber.*, **12**, 698—699).—Five parts by weight of cooled nitric acid (sp. gr. 1·5) are gradually rubbed up with one part of mannite. The solution is poured into a well cooled vessel and mixed with ten parts of sulphuric acid. The semi-solid mass is filtered and the residue well washed with water, and finally with soda-solution. To obtain the nitromannite in a pure state it must be repeatedly crystallised from alcohol. It then consists of

long white needles which melt at 112—113°, and are decomposed at a higher temperature. The sp. gr. of the crystals at 0° is 1·604, of the fused compound 1·446—1·537. In contact with a glowing wire or a gas flame, nitromannite melts but does not burn. If it is thrown on glowing coals it first melts and then explodes. It may be pressed and rubbed up in a porcelain mortar without danger. It may be cut or sawn when compressed. Under the blow of a hammer it explodes more violently than mercury fulminate: it is also exploded by the action of various fulminates.

Nitromannite compressed into a metal capsule explodes by the action of fulminates, only when a certain quantity of the powdered compound is also present. Contained loosely in capsules not sealed up, it explodes only by the action of diazobenzene nitrate. The author concludes from his experiments that the explosion of nitromannite is produced only by a certain determinate vibration. G. T. A.

Compounds of Grape-sugar with Cupric Hydrate. By E. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 704).—When solutions of 1 mol. of grape-sugar, 5 mols. of copper sulphate, and 11 mols. of sodium hydrate are mixed together so that the mixture does not contain less than 0·5—1·0 per cent. of sugar, and filtered, the solution is free from sugar. The author maintains, in opposition to Müller and Hagen (*Pfluger's Arch.*, **17**, 568), that the precipitate contains the sugar in chemical combination, and shows that it is perfectly soluble in excess of caustic soda. G. T. A.

Transformation of Sugar into Alcohol by a Purely Chemical Method. By Berthelot (*Ann. Chim. Phys.* [5], **17**, 450—451).—Two cylinders of spongy platinum were connected with the terminals of a battery of six or eight Bunsen cells, an oscillating commutator being arranged in the circuit in such a way that the electrodes were made alternately positive or negative twelve or fifteen times per second. This arrangement was so adjusted that when the cylinders were placed in acidulated water no gas was evolved. The electrodes were then transferred to an aqueous solution of glucose. The simultaneous oxidations and reductions of the glucose gave rise to the formation of small quantities of alcohol. By far the greater part of the sugar remained, however, unaltered. C. H. B.

The Carbohydrates of the Jerusalem Artichoke. By E. Dieck and B. Tollens (*Bied. Centr.*,* 1879, 276—281).—It has long been known that the tubers of the Jerusalem artichoke contain considerable quantities of inulin and of a gum called levulin. The authors have made a further investigation of this last-named body, and find that its formula is expressed by a multiple of $C_6H_{10}O_5$. By warming with dilute acid it is converted into a sugar, which does not turn the plane of polarisation so strongly to the left as that prepared from inulin. This sugar is also easily fermentable, and the author is of

* Biedermann's *Centralblatt für Agriculturchimie und Landwirthschaftsbetrieb*, Leipzig, Verlag von Hugo Voigt.

opinion that the tubers may be used with advantage for preparing alcohol. J. K. C.

A New Carbohydrate. By O. Schmiedeberg (*Deut. Chem. Ges. Ber.*, **12**, 704—705).—A carbohydrate very much resembling achroodextrin in external appearance is found in abundance in the squill (*Urginea scilla*). It is, however, lævogyrate, and is converted almost entirely into levulose by the action of warm dilute acids. The author proposes the name of *sinistrin* for this new body. It may be obtained by adding lead acetate to powdered squill, made into a thin paste with water, as long as a precipitate is formed. The filtrate, after removal of lead, is mixed with excess of calcium hydrate, which precipitates the sinistrin. The precipitate is decomposed by carbonic anhydride, and any lime remaining in the liquid is removed by careful addition of oxalic acid. The filtrate is then decolorised by animal charcoal, gently evaporated at 40—50°, and the sinistrin precipitated by alcohol. Pure sinistrin, $C_6H_{10}O_5$, is colourless and amorphous: it dissolves in water in all proportions, and in presence of an alkali holds copper oxide in solution without reducing it. Its specific rotatory power is $[\alpha]_D = -41{\cdot}4°$. Saliva and diastase have no action on sinistrin, but warm dilute sulphuric acid completely converts it into sugar consisting of a mixture of lævulose with an optically inert variety, both of which are capable of fermentation, and reduce copper oxide in alkaline solution. G. T. A.

Hydrocellulose. By A. Girard (*Compt. rend.*, **88**, 1322—1324).—When substances consisting mainly of cellulose, such as cotton, flax, hemp, &c., are subjected to the action of a current of gaseous hydrochloric, hydrobromic, hydriodic, or hydrofluoric acid, hydrocellulose is formed. This change is accompanied by an elevation of temperature. The vapours of sulphuric and nitric acids produce the same effect, but sulphurous anhydride and sulphuretted hydrogen have no action. The time required for the conversion of the cellulose into hydrocellulose depends on the porous nature of the material used. With some very porous substances the change is complete in a few minutes. This reaction takes place only in the presence of moisture. If the gas and the substance operated on be perfectly dry, no hydrocellulose is formed, even after the lapse of some time. C. H. B.

Tetrallyl-ammonium Bromide and Triallylamine. By H. Grosheintz (*Bull. Soc. Chim.* [2], **31**, 390—391).—*Tetrallyl-ammonium Bromide.*—To prepare this body in large quantities, ammonia gas is passed into an alcoholic solution of allyl bromide. The whole mass crystallises, and is exhausted with a mixture of ether and absolute alcohol. This solution on evaporation in a vacuum deposits small white crystals of tetrallyl-ammonium bromide; it is soluble in water and alcohol, and sparingly soluble in ether. It decomposes at 80°. With platinum chloride it forms a chlorobromide, which is very soluble in water.

By adding water to the mother-liquor from the crystals obtained during the passage of ammonia gas into the solution, an oil separates

out, boiling at 85°, which apparently consists of ethyl-allyl ether. It forms a crystalline compound with silver nitrate.

Triallylamine is obtained, by the dry distillation of tetrallyl-ammonium bromide with potash, as a yellowish liquid lighter than water. It has a very disagreeable penetrating odour and an alkaline reaction. Its hydrochloride forms a double compound with platinum chloride, sparingly soluble in water. L. T. O'S.

Bases derived from Aldol-ammonia. By A. Wurtz (*Compt. rend.*, 1879, **88**, 1154—1158).—By heating aldol with excess of aqueous ammonia at 140—180°, a crystalline substance is obtained, having the composition $C_{12}H_{24}N_4$. The same body is more easily obtained by heating crotonaldehyde with a large excess of ammonia in sealed tubes to 100°. As a considerable amount of heat is evolved by the reaction, the two substances must be mixed with care. The reaction may be represented thus: $3C_4H_6O + 4NH_3 = C_{12}H_{24}N_4 + 3H_2O$.

Tricrotonylenamine, $(C_4H_6)_3N_4H_6$, crystallises in colourless, brilliant, orthorhombic prisms, which contain $6H_2O$, and effloresce on exposure to the air. They lose their water at 100°, and are sparingly soluble in cold, freely in hot water. They are also readily soluble in alcohol. Heated cautiously in an open vessel, the base sublimes unchanged, but in a closed vessel it decomposes with evolution of ammonia; hence its vapour-density cannot be determined. Under a pressure of 0·04 m. it appears to distil at 190°. Heated with an excess of hydrochloric acid at 150°, the base loses its ammonia, and is converted into a resinous mass, consisting probably of partially dehydrated and polymerised crotonaldehyde.

Tricrotonylenamine forms several series of salts, which crystallise with difficulty from neutral, but easily from acid solutions.

The *hydrochloride*, $C_{12}H_{24}N_4.3HCl$, and the *nitrate*, $C_{12}H_{24}N_4.3HNO_3$, crystallise in hexagonal prisms. They are soluble in water, and have a strongly acid reaction. Two *chloroplatinates* have been obtained, having the formulæ $C_{12}H_{24}N_4.3HCl.2PtCl_4$ and $(C_{12}H_{24}N_4.4HCl)_2.3PtCl_4$ respectively. Three crystalline *chloro-aurates* have been prepared, viz.,

$C_{12}H_{24}N_4.4HCl.AuCl_3$, $C_{12}H_{24}N_43HCl.AuCl_3 + 2H_2O$, and $(C_{12}H_{24}N_4.4HCl)_2.5AuCl_3$. C. H. B.

Action of Sulphuric Acid on Acetylene. By G. Lagermark and A. Eltekoff (*Deut. Chem. Ges. Ber.*, **12**, 693—694).—The assertion of the authors (*Ber.*, **9**, 637) that crotonaldehyde is produced by the action of sulphuric acid on aldehyde was contradicted by Berthelot and Zeisel, who attributed its formation to the presence of vinyl bromide in the acetylene. The authors, having made further experiments, show that this is not the case, and that their crotonaldehyde (prepared by the action of zinc chloride on acetaldehyde) is identical with Berthelot's supposed vinyl alcohol. G. T. A.

Substituted Nitrogen Chlorides. By K. Köhler (*Deut. Chem. Ges. Ber.*, **12**, 770—772).—Tscherniak (*Ber.*, **11**, 143) has shown that triethylamine is produced by the action of zinc-ethyl on ethyl-

nitrogen chloride, thus proving that the chlorine in the latter compound is directly combined with the nitrogen. The author confirms these results, and finds that ethyl-nitrogen chloride boils at 86—91°. He has also prepared *methyl-nitrogen chloride* by a method analogous to that proposed by Tscherniak for the ethyl-compound. This substance is a golden-yellow liquid (b. p. 60° uncor.) of penetrating smell, producing tears. On long standing it deposits a crystalline substance, which could not be investigated from want of material; it, however, contains a large quantity of chlorine, and is decomposed by water, with evolution of gas and formation of methyl-nitrogen chloride. This last compound is quite as stable as the corresponding ethyl compound. It is not decomposed by either cold or hot water, nor does it yield a tetrachloride with chlorine even at −20°. It decomposes hydrogen sulphide with separation of sulphur. It has been previously shown (Michaelis and Köhler (*Ber.*, **10**, 807) that phospho-benzene, analogous to azo-benzene, is obtained by the action of phenyl-phosphine on phosphenyl chloride. The author is at present engaged in trying whether a similar reaction occurs with the substituted ammonias and nitrogen chlorides of the fatty series, with the formation of the corresponding azo-compounds. T. C.

Diguanidine. By B. Rathke (*Deut. Chem. Ges. Ber.*, **12**, 776—784).—In a former communication (*Ber.*, **11**, 967) the author described the production of a new base as a bye-product in the action of phosphorus trichloride on thiocarbamide, but owing to the small quantity obtained he was unable to investigate it completely. It is now found that this substance is a di-acid base, *diguanidine*, $NH:C(NH_2).NH.C(NH_2):NH$. It can also be obtained by digesting a mixture of thiocarbamide and guanidine thiocyanate with phosphorus trichloride or bromine. Diguanidine and its salts are colourless. The free base and its carbonate give a strongly alkaline reaction. The sulphate, $C_2N_5H_7.H_2SO_4 + H_2O$, forms rhombic crystals, which are easily soluble in water. The hydrochloride and nitrate also crystallise in needles and are very soluble in water. The platinum salt, $C_2N_5H_7.2HCl + PtCl_4 + 2H_2O$, loses its water of crystallisation at 100°. The most characteristic property of diguanidine is that both the base and its salts exchange an atom of hydrogen for one of copper, by which its saturating capacity is reduced by one-half. The salts of this copper compound form silky rose-red crystals, which are almost insoluble in water and are decomposed only by the strongest bases. The free copper base, $C_2N_5H_6Cu' + H_2O$, is brick-red, and although insoluble in cold water, is far more soluble in hot water than its salts. From the hot aqueous solution, to which it imparts an amaranth-red, it separates in glistening quadratic plates. It loses its water of crystallisation at 100°, but readily takes it up again on exposure. The relation of diguanidine to biuret and dicyandiamine is shown as follows:—

Biuret.....	$O:C(NH_2).NH.C(NH_2):O$
Dicyandiamine	$NH:C(NH_2).NH.C(NH_2):O$
Diguanidine	$NH:C(NH_2).NH.C(NH_2):NH$

Diguanidine is distinguished from the other two bases by the fact that its copper compound has basic properties, and that the salts of this copper compound are not decomposed by ammonia. T. C.

Melissic Acid. By Schalfeeff (*Deut. Chem. Ges. Ber.*, **12**, 697).—The author has convinced himself that neither melissene (myricylene) nor melissic acid is a simple chemical compound. By crystallisation from ether melissene can be separated into several bodies melting at from 83—84° to 87—88°. Melissic acid under similar treatment yields a series of compounds melting between 85 and 91°. It is shown from the form of the crystals and the melting points that melissic acid has some compounds in common with cerotic acid. The composition of the constituents of melissic acid has not yet been determined.

G. T. A.

Dimethylacrylic Acid an Isomeride of Angelic Acid. By E. Duvillier (*Compt. rend.*, **88**, 1209).—The author acknowledges the prior claim of v. Miller to the discovery of this acid, but points out that whilst Miller prepared it by oxidising valeric acid or isobutylformic acid, he himself obtained it by the action of sodium ethylate on ethyl bromo-isovalerate. C. H. B.

Synthesis of Tetrolic Acid. By G. Lagermark (*Deut. Chem. Ges. Ber.*, **12**, 853—854).—Dry allylene, obtained from bromopropylene, is absorbed in large quantities when passed into ether placed in a freezing mixture. Sodium acts on this solution with evolution of hydrogen and formation of sodium-allylene, C_3H_3Na. This latter compound is a white crystalline powder, which is insoluble in ether, and is so rapidly attacked by carbonic anhydride that carbonisation takes place if the gas be not passed in a very slow stream; in the latter case, however, *sodium tetrolate*, $C_4H_3O_2Na$, is formed. The free acid, which the author considers to be identical with that obtained by Geuther from monochlorcrotonic acid, crystallises in colourless transparent tables (m. p. 76°, b. p. 197—205°, with partial decomposition), which are easily soluble in water, alcohol, and ether. It is scarcely volatile with steam, and combines directly with bromine to form a liquid compound which afterwards becomes crystalline, hydrobromic acid being evolved. Almost all the salts of tetrolic acid are soluble. An attempt to determine the vapour-density of the acid at the temperature of boiling ethyl benzoate showed that at this temperature it was completely decomposed into allylene and carbonic anhydride.

T. C.

Fermentation of Hydroxyvaleric Acid. By P. Giacosa (*Deut. Chem. Ges. Ber.*, **12**, 703).—Calcium hydroxyvalerate and decaying fibrin yielded at the end of three months, besides calcium carbonate, an acid which was probably a mixture of butyric and valeric acids.

G. T. A.

Preparation of Malonic Acid. By E. Grimaux and J. Tcherniak (*Bull. Soc. Chim.* [2], **31**, 338—340).—The method consists in the conversion of chloracetic acid into cyanacetic acid, which, when subjected to the action of hydrochloric acid, yields malonic acid.

When 250 grams of chloracetic acid dissolved in 500 grams of water

are saturated with anhydrous sodium carbonate, and mixed with a solution of potassium cyanide containing 200 grams KCN in 200 H_2O, double decomposition takes place, potassium chloride and cyanacetic acid being formed. The solution is neutralised with sulphuric acid and exhausted with ether. On evaporating the ethereal solution a syrupy residue of cyanacetic acid is left. This residue is mixed with three times its volume of concentrated hydrochloric acid and heated in a water-bath for seven or eight hours, hydrochloric acid gas being passed through the solution. The contents of the glass are then distilled in a vacuum; the residue is exhausted several times with ether; and the ethereal extracts are mixed together. On evaporation they yield crystals of malonic acid melting at 102°. The yield of malonic acid equals 34 per cent. of the weight of chloracetic acid. L. T. O'S.

Synthesis of Isosuccinic Acid. By H. Züblin (*Deut. Chem. Ges. Ber.*, **12**, 1112).—Ethyl isosuccinate is formed by treating the product of the action of sodium on ethyl malonate with methyl iodide, $NaHC(COOEt)_2 + MeI = CHMe(COOEt)_2 + NaI$. The acid was obtained by the saponification of the ethereal salt. W. C. W.

Derivatives of Mucic Acid. By E. Seelig (*Deut. Chem. Ges. Ber.*, **12**, 1081—1092).—*Dehydromucic acid*, $C_6H_4O_5$, separates out when mucic acid is heated in sealed tubes at 130—140° with concentrated hydrobromic acid, or at 140—150° with fuming hydrochloric acid. The crude product is treated with boiling water, in which the dehydromucic acid is more readily soluble than the mucic acid. On cooling the aqueous solution, the hydromucic acid is deposited in colourless needles or plates.

$BaC_6H_2O_5 + 2\frac{1}{2}H_2O$ separates in hard crystals when a hot concentrated solution of the salt is allowed to cool slowly, but when the hot solution is suddenly cooled, soft needle-shaped crystals containing $6H_2O$ are obtained.

Two new acids are formed by the action of sodium-amalgam on a dilute solution of dehydromucic acid. They are separated by the following process:—The alkaline liquid from which the mercury has been removed by decantation is neutralised with sulphuric acid and evaporated to dryness. The residue is powdered in a mortar, transferred to a stoppered bottle, and treated with dilute sulphuric acid and ether. On evaporating the ethereal extract, a syrupy liquid remains, soluble in water. The aqueous solution slowly deposits a soft mass of crystals when exposed in a vacuum over sulphuric acid.

When the mixture of acids is neutralised with barium carbonate, needle-shaped crystals having the composition $BaC_6H_4O_5 + 4\frac{1}{2}H_2O$, separate out. On attempting to purify this salt by recrystallisation from hot water, a portion of it is invariably converted into a transparent crystalline powder containing 2 mols. H_2O. The mother-liquor from the first crop of crystals yields on further concentration an opaque white mealy deposit composed of microscopic needles, $BaC_6H_4O_5 1\frac{1}{2}H_2O$. On evaporating to dryness the filtrate from these crystals, an amorphous mass remains which resembles dextrin in appearance.

The acid $C_6H_8O_5$ is obtained in soft, thin, white plates (m. p. 146°) soluble in water, alcohol, and ether, by the action of dilute sulphuric acid on the needle-shaped barium salt. From the mealy salt an acid forming hard transparent crystals, $C_6H_6O_5.H_2O$ (m. p. 173°), is obtained. Both acids taste like tartaric acid. The soft acid forms a silver salt, $Ag_2C_6H_4O_5.\frac{1}{2}H_2O$, crystallising in microscopic needles. It detonates at 200°. The calcium salt, $CaC_6H_4O_5.3\frac{1}{2}H_2O$, also forms microscopic needles.

The hard acid, $C_6H_6O_5.H_2O$, yields a silver salt having the composition $Ag_2C_6H_4O_5$, which detonates at 160°. It resembles the silver salt of the soft acid in appearance. The calcium salt, $CaC_6H_4O_5.1\frac{1}{2}H_2O$, on evaporation over sulphuric acid, separates out as a gelatinous mass insoluble in alcohol. W. C. W.

Thiamides of the Oxalic Acid Series. By O. Wallach and P. Pirath (*Deut. Chem. Ges. Ber.*, **12**, 1063—1065).—The action of phosphorus pentachloride on diethyloxamide takes place in two stages, viz., the two substances first liquefy, and then on gently warming the mixture a copious evolution of hydrochloric acid takes place. If the operation is interrupted at the end of the first stage, and sulphuretted hydrogen is passed into the well-cooled liquid previously diluted with benzene, until hydrochloric acid ceases to be given off, large reddish-yellow transparent plates of *thiodiethyloxamide* will be deposited when the benzene evaporates. The formation of this compound shows that the oxygen in the diethyloxamide has been completely replaced by chlorine; the following reaction then takes place between the amido-chloride and the sulphuretted hydrogen:—

$$EtHN.Cl_2C.CCl_2.NHEt + 2H_2S = 4HCl + EtHN.SC.CS.NHEt.$$

Thiodiethyloxamide melts at 54°. When treated with sodium-ethylate and ethylbromide it yields an oily liquid boiling above 250°, which probably has the composition $EtN : C(SEt).C(SEt) : NEt$, but was not obtained in a state of purity.

By treating the product of the action of phosphorus pentachloride on oxanilide with sulphuretted hydrogen a compound is obtained which is deposited from an ethereal solution in golden plates.

W. C. W.

Pseudouric Acid. By E. Grimaux (*Bull. Soc. Chim.* [2], **31**, 535—536).—By heating a mixture of equal parts of uramil and urea at 180° ammonia is eliminated, and the ammonium salt of an acid is obtained corresponding with Baeyer's pseudouric acid, $C_5H_6N_4O_4$. On passing carbonic anhydride through a solution of the ammonium salt in caustic soda the sodium salt separates out. Pseudouric acid may be easily obtained from a solution of this salt by precipitating it with hydrochloric acid. That it is identical with Baeyer's acid, is shown by the analysis of the barium salt, which crystallises with $5H_2O$ and loses all its water at 150°. It is uric acid plus the elements of water, and all attempts to eliminate the latter have failed. Phosphorus oxychloride has no action on the acid; sulphuric acid attacks it only at 150°, decomposing it with formation of carbonic anhydride, ammonium sulphate, and xanthinine, $C_4H_3N_3O_2$; the latter compound is

also obtained by the action of heat on ammonium thionurate (Finck, *ibid.*, **4**, 224). The formation of xanthinine from pseudouric acid is represented thus: $C_5H_6N_4O_4 + H_2SO_4 = C_4H_3N_3O_2 + (NH_4)HSO_4 + CO_2$.

L. T. O'S.

Interpretation of Reactions Occurring in Presence of Aluminium Chloride. By G. Gustavson (*Deut. Chem. Ges. Ber.*, **12**, 853).—The author, by means of the results obtained by Adrianowsky, endeavours to explain the reaction which Friedel and Crafts have found to occur between acid anhydrides, benzene, and aluminium chloride. The part which aluminium chloride plays in these reactions consists, partly in its combination with benzene to form $Al_2Cl_6.6C_6H_6$ and partly in the conversion of the acid anhydrides into chlorine compounds, which latter react on the $Al_2Cl_6.6C_6H_6$, with evolution of hydrochloric acid.

T. C.

Compounds of Cymene with Aluminium Bromide and Chloride. By G. Gustavson (*Deut. Chem. Ges. Ber.*, **12**, 694—695).—These compounds, $Al_2Br_6.3(C_{10}H_{14})$ and $Al_2Cl_6.3(C_{10}H_{14})$, are formed by passing the hydracids into solution of Al_2Br_6 and Al_2Cl_6 in cymene, and consist of transparent, reddish-brown, thick liquids. The first has a sp. gr. of 1·493 at 0°, and 1·477 at 16°, is decomposed by water, and reacts very energetically with bromine, yielding pentabromotoluene and isopropyl bromide. The second has a sp. gr. of 1·139 at 0°, and 1·127 at 18°, is decomposed by water, and reacts energetically with bromine and chlorine.

G. T. A.

Action of Ethylene on Benzene in presence of Aluminium Chloride. By Balsohn (*Bull. Soc. Chim.* [2], **31**, 529—542).—On passing dry ethylene and hydrochloric acid into a mixture of benzene and aluminium chloride, the ethylene is absorbed, and a liquid obtained boiling at the same temperature as ethyl-benzene.

If ethylene alone is passed into the same mixture hydrochloric acid gas is evolved, but the evolution ceases after a time. After the ethylene has been passed through the mixture for a sufficient length of time, at a temperature of 70—90°, it is poured into water. The hydrocarbon separated from the water and fractionally distilled, is found to consist of a mixture of ethyl-benzene, diethyl-benzene, and triethyl-benzene. The higher-boiling portions were not examined, but it is possible that they consist of more highly ethylated benzenes. The reaction in the first case, when ethylene and hydrochloric acid gas are passed into a mixture of benzene and aluminium chloride, may be explained by supposing that first the two gases act on one another and form ethyl chloride, which then acts on the benzene in presence of aluminium chloride, forming ethyl-benzene in the manner described by Friedel and Crafts.

Aluminium chloride at a gentle heat combines with ethylene, forming a liquid which is decomposed by the action of water, giving rise to thick oily products having the odour of terebenthene.

L. T. O'S.

Aniline Salts. By M. Beamer and F. W. Clarke (*Deut. Chem. Ges. Ber.*, **12**, 1066—1067).—*Aniline chlorate* is deposited on evapo-

rating the alcoholic solution in a vacuum, in long white prisms soluble in ether. This salt decomposes on exposure to the air; it explodes by percussion, and also when heated to 75°. *Aniline perchlorate* crystallises in large rhombic plates. It is more stable than the chlorate, but explodes when heated. The *iodate* separates out of an alcoholic solution in pearly scales (sp. gr. 1·48 at 13°), which are soluble in hot water. The salt blackens without explosion if gradually heated, but if it is suddenly exposed to a temperature of 130° it explodes. *Aniline hydrofluoride* forms pearly scales soluble in hot alcohol. *Aniline phthalate* crystallises in needles (m. p. 145°). *Aniline monochloracetate* forms thin white needles which melt at 88°, and the *dichloracetate* crystallises in white prisms (m. p. 122°). The *trichloracetate* is deposited from a concentrated aqueous solution in thin transparent rhombic plates, which become opaque at 50° and melt at 145°.

W. C. W.

Thio-derivatives. By O. Wallach and H. Bleibtreu (*Deut. Chem. Ges. Ber.*, **12**, 1061—1063).—The authors have succeeded in preparing the homologues of ethylisothiacetanilide, $CH_3.C(SEt):NC_6H_5$ (*Ber.*, **11**, 1590), and by treating these compounds with the theoretical amount of a dilute mineral acid they have obtained the ethereal salts of thioacetic acid.

	Boiling point.
Methylisothiacetanilide	244—246°
Ethylisothiacetanilide	255—257
Propylisothiacetanilide	270—273
Isopropylisothiacetanilide	—
Allylisothiacetanilide	Boils above 260° with decomposition
Isobutylisothiacetanilide	Decomposes on boiling
Methyl thiacetate	95—96
Ethyl thiacetate	115—117
Propyl thiacetate	135—137
Isopropyl thiacetate	124—127
Isobutyl thiacetate	148—150

Ethenyldiphenylamidine is formed when ethyl-isothiacetanilide is boiled with oxalic acid. It is also formed together with mercaptan, by the action of ethyl-isothiacetanilide on aniline, $CH_3.C(SEt):NPh + NH_2Ph = CH_3.C(NHPh):NPh + SHEt$.

Substituted amidines can be obtained by gently warming the isothiacetanilide with aniline hydrochloride. W. C. W.

Homologous Tertiary Diamines obtained in the Methylaniline Manufacture. By O. Doebner (*Deut. Chem. Ges. Ber.*, **12**, 810—814).—In the manufacture of methylaniline, there is produced, under certain conditions, a series of crystalline diamines, which are non-volatile in steam, and one member of which, viz., $C_{19}H_{26}N_2$, has been investigated by Hofmann and Martius (*Ber.*, **6**, 345). The crude material employed in the present investigation was obtained under abnormal conditions in the manufacture of malachite green. From this product, a pure base was prepared by repeated crystallisa-

tion from alcohol in the form of shining plates (m. p. 90°), which are insoluble in water, difficultly soluble in cold, but more easily soluble in hot alcohol, easily soluble in ether, benzene, and carbon bisulphide. It dissolves in acids and is reprecipitated by alkalis. On oxidation it gives a strong smell of quinone, the liquid becoming blue and afterwards yellowish-brown. The new base has the composition $C_{17}H_{22}N_2$, and is a lower homologue of the base $C_{19}H_{26}N_2$, which it resembles in most of its properties. The hydriodide, $C_{17}H_{22}N_2.2HI$, crystallises in tables which are rather insoluble in cold water.

The base may be prepared synthetically by the action of methylene iodide on dimethyl-aniline, thus:—

$$CH_2I_2 + 2C_8H_{11}N = H_2C(C_6H_4.NMe_2)_2 + 2HI.$$

Its composition is therefore as represented in the equation (see also *Ber.*, **12**, 681). The homologous base $C_{19}H_{26}N_2$ (*vide supra*) may also be obtained in a similar manner by the action of acetone on dimethyl-aniline, thus: $COMe_2 + 2C_6H_5.NMe_2 = Me_2.C.(C_6H_4.NMe_2)_2 + H_2O$.

T. C.

Remarks on Doebner's Communication "On Malachite-green." By E. and O. Fischer (*Deut. Chem. Ges. Ber.*, **12**, 791—796).

Reply to the Remarks of E. and O. Fischer on "Malachite-green." By O. Doebner (*ibid.*, **12**, 1010).—A personal discussion as to the priority of the discovery of malachite-green.

Dyes of the Rosaniline Group. By E. and O. Fischer (*Deut. Chem. Ges. Ber.*, **12**, 796—803).—*Benzaldehyde green* is obtained from the leuco-base (prepared from bitter-almond oil) by treating the dilute sulphuric acid solution with manganese dioxide. It may be purified by means of the zinco-chloride, which is very difficultly soluble in cold water, and in the pure state crystallises in brilliant green plates. On addition of ammonia the free base is obtained from this compound in flocks, which crystallise from alcohol in aggregates of colourless prisms. An analysis of the picrate gave 62·04 C and 5·05 H, agreeing very nearly with that of the corresponding compound of malachite-green by Doebner. Like the latter, it crystallises from hot benzene in golden needles. The other salts of the base likewise resemble those of malachite-green. The reduction-products of the two dye-stuffs also agree in melting point and crystalline form. The two are therefore probably identical.

A third dye-stuff, which appears to be identical with the other two, is obtained by the action of benzoic chloride on dimethylaniline in presence of zinc chloride. Another product (m. p. 38°) of this reaction is identical with that obtained by O. Fischer (*Ber.*, **10**, 958) from benzoic acid, dimethylaniline, and phosphorus pentoxide.

Benzaldehyde green on reduction with zinc and hydrochloric acid yields a leuco-base, which crystallises from alcohol in silky needles (m. p. 102°), and is identical with the leuco-base (m. p. 101°) obtained by Doebner from malachite-green, and also with tetramethyldiamidotriphenylmethane. This leuco-base exists in three isomeric modifications, one of which crystallises in monoclinic or triclinic needles

(m. p. 102°), another in triclinic symmetric plates (m. p. 93°), and the third in fine radial sphœrocrystals of still lower melting point. Crystals of all three modifications may be obtained if the fused substance is allowed to solidify slowly at 70—80°.

Paranitrobenzaldehyde green is obtained by acting on a mixture of 1 mol. paranitrobenzoic chloride and 2 mols. dimethylaniline with $\frac{1}{2}$ mol. of zinc chloride. It crystallises from hot alcohol in fine golden-yellow prisms. Analysis gave 71·1 C and 6·8 H, agreeing nearly with the formula $C_{22}H_{21}N_3O_2 + C_2H_6O$. The presence of alcohol of crystallisation was, however, not directly proved. The compound is probably an ethyl-ether, analogous to rosaniline hydrate. It dissolves in dilute mineral acids with a green colour, which is turned dark yellow by strong acids. In acetic acid solution it dyes silk and wool a beautiful green. The picrate consists of fine microscopic needles, which are very difficultly soluble in benzene, but more easily soluble in hot alcohol. It differs from the corresponding compound of benzaldehyde green in its smaller solubility, in the yellow colour of the free base, and its lower basicity. On reduction with zinc-dust in acidified alcoholic solution the green colour changes first to blue-violet and then to red-violet. The substance thus produced dyes wool and silk like the violet derivative of rosaniline. On further reduction a leuco-base is obtained, which on oxidation is reconverted into the violet. The base is probably a methylated leucaniline, the transformation of the green nitro-compound into the violet being quite analogous to the formation of rosaniline from trinitrotriphenylcarbinol. It is probable that in methyl-violet the third amido-group present in the para-position alone causes the difference of colour from that of benzaldehyde green.

Metanitrobenzaldehyde green, $C_{23}H_{25}(NO_2)N_2$, is obtained by the oxidation of the nitrotetramethyl-diamidotriphenylmethane prepared from metanitrobenzaldehyde and dimethylaniline. It crystallises from alcohol in yellow prisms (m. p. 152°). It is somewhat difficultly soluble in ether, alcohol, and light petroleum, but easily in benzene. It dissolves in acids to form colourless salts. The picrate, $C_{29}H_{26}N_6O_9$, crystallises from alcohol or benzene in aggregates of small green needles. On reduction in a manner similar to that employed in the case of the para-compound, no trace of violet is obtained, for the green colour gradually disappears with formation of a crystalline leuco-base, which on oxidation is reconverted into a green dyestuff. The tetramethyl-triamidotriphenyl-methane,

$$NH_2.C_6H_4.CH(C_6H_4.NMe_2)_2,$$

obtained from nitrotetramethyl-diamidotriphenylmethane by reduction with zinc and hydrochloric acid behaves in a manner similar to metanitrobenzaldehyde green, and, like the latter, crystallises in aggregates of colourless needles (m. p. 130°). On heating the leuco-base with methyl iodide and methyl alcohol at 120°, an ammonium compound is produced which corresponds with the methylated paraleucaniline obtained by Hofmann. The iodide crystallises with very great difficulty, and is very soluble in water. An analysis of the platinum salt led to the formula $2C_{19}H_{13}[NMe_3Cl]_3.3PtCl_4$. The dry

iodide heated in contact with air gives methyl iodide and a green dye-stuff. If methylated leucaniline (which is obtained from pure pararosaniline by Hofmann's method, and must be considered as a derivative of the triamido-base containing nine methyls) be heated in a similar manner, only methyl-violet is obtained. This proves that the nature of the dye-stuff produced depends on the position of the single amido-groups. T. C.

Lithium Picrate. By M. Beamer and F. W. Clarke (*Deut. Chem. Ges. Ber.*, **12**, 1068).—This salt is deposited from an alcoholic solution in pale yellow prisms, sp. gr. 1·740 at 20°. The crystals explode on percussion, and also when suddenly heated. W. C. W.

Formation of Cresols during Putrefaction. By E. Baumann and L. Brieger (*Deut. Chem. Ges. Ber.*, **12**, 706).—Investigation of a large quantity of phenol formed during putrefaction of albumin showed that it consisted chiefly of paracresol. In addition to paracresol, some phenol was obtained from the mixture in the form of potassium paraphenolsulphonate, together with traces of orthocresol. The formation of cresols during the putrefaction of albumin explains the occurrence of the corresponding sulphonic acids in urine, and is the only source of these latter bodies in the animal system. G. T. A.

Paracresol. By E. Baumann and L. Brieger (*Deut. Chem. Ges. Ber.*, **12**, 804—806).—When bromine-water is added to an aqueous solution of pure paracresol until a permanent colour is obtained, a cloudiness is first produced, and in a short time crystalline plates of tetrabromoparacresol are deposited, which, after rapid filtering and drying over sulphuric acid, melt at 109°. This substance, on keeping, gradually undergoes decomposition. The yield of the bromophenol is always less than the calculated quantity.

If the precipitate formed by bromine-water in a solution of paracresol be allowed to stand over night in contact with bromine-water, the amount of bromine in the precipitate is lowered by about 2 per cent., and the melting point becomes less than 100°. This is caused by the gradual evolution of carbonic anhydride, and simultaneous production of tribromophenol (m. p. 91°), which takes place much more rapidly and completely when the temperature is raised to 30—40°.

These facts show that in all previous determinations of the phenol in urea, &c., by means of bromine-water, the results have been too low, and that the method cannot be used with any degree of exactness.

T. C.

Aurin. By P. de Clermont and J. Frommel (*Bull. Soc. Chim.* [2], **31**, 340—341).—The authors' experience has led them to the conclusion that the formation of aurin from phenol is due to the action of carbonic acid: the carbonic acid in the nascent state reacting with the phenol to produce a compound of the formula $(C_6H_4.OH)_2C<\begin{matrix}O\\|\\O\end{matrix}>C_6H_4$.

L. T. O'S.

Derivatives of Methyl-Eugenol. By M. Wassermann (*Compt. rend.*, **88**, 1206—1209).—*Monobromomethyleugenyl Dibromide*—

$$C_6H_2Br(OMe)_2.C_3H_5Br_2,$$

is obtained by the action of bromine on a strongly cooled solution of methyl-eugenol in ether. It crystallises in long, silky needles, which melt at 77—78°, and are soluble in alcohol and ether.

Monobromomethyleugenol, $C_6H_2Br(OMe)_2.C_3H_5$, is prepared by the action of zinc-dust on a hot alcoholic solution of the preceding compound. It is a colourless liquid which boils at 190°, under a pressure of 0·02 m., and is soluble in alcohol, ether, and acetic acid.

Methyleugetic Acid, $C_6H_2(OMe)_2.C_3H_5COOH$, is obtained by the action of sodium amalgam and chlorocarbonic ether on monobromomethyleugenol. It crystallises in flat, yellowish needles, which fuse at 180°. They are soluble in alcohol and ether, and are slightly soluble in water.

Mercurdimethyleugenol $(C_{11}H_{13}O_2)_2Hg$. This substance is formed if an excess of sodium-amalgam is used in the preparation of the preceding acid. It crystallises in colourless needles, soluble in alcohol and ether, and fusing at 140°.

By heating an alkaline solution of methyleugetic acid with a solution of potassium permanganate, acidulating, and agitating the concentrated liquid with ether, a substance is obtained having the formula $C_{12}H_{12}O_3$. Its constitution is probably—

$$C_6H_2(OMe)_2(CH:CH.CHO).COOH.$$

It forms colourless needles, soluble in water and fusing at 162—163°. In no case was any opianic acid formed. C. H. B.

Synthesis of Deoxybenzoïn. By C. Graebe and H. Bungener (*Deut. Chem. Ges. Ber.*, **12**, 1079—1080).—By the action of aluminium chloride on a mixture of benzene and phenylacetic chloride, deoxybenzoïn (m. p. 57°) is obtained—

$$C_6H_5.CH_2.COCl + C_6H_6 = C_6H_5.CH_2.CO.C_6H_5 + HCl.$$

The phenylacetic chloride used in this experiment was prepared by carefully mixing phenylacetic acid and phosphorus pentachloride. In order to remove the phosphorus oxychloride which is formed as a by-product, the mixture is heated at 110—120° in a stream of carbonic anhydride. W. C. W.

Nitro- and Amido-Derivatives of Deoxybenzoïn. By P. Goldbeff (*Deut. Chem. Ges. Ber.*, **12**, 693).—The author adds the following to his contribution to the *Berichte*, **11**, 1939. Mononitrodesoxybenzoïn crystallises in four-sided prisms, which generally assume the form of thick plates. It is soluble in 22·5 parts of boiling and 5·97 of cold alcohol (95 per cent.), easily in acetic acid, tolerably well in light petroleum, with difficulty in boiling, sparingly in cold ether, and not at all in water. It melts at 140—142°, and is decomposed on distillation. It yields with alkalis, especially in presence of alcohol, a violet

colour. It is oxidised by chromic acid, into benzoic and nitrobenzoic acids. The chloroplatinate of monamidodesoxybenzoïn—

$$(C_{11}H_{14}ON)_2PtCl_6,$$

crystallises in large, hexagonal, orange-coloured prisms.

G. T. A.

Benzal Sulphide and Thiobenzaldehyde. By C. Böttinger (*Deut. Chem. Ges. Ber.*, **12**, 1053—1057).—An alcoholic solution of benzal sulphide undergoes no change on boiling with concentrated hydrochloric or hydrocyanic acids; but when benzal sulphide is gently heated in a silver dish with a concentrated solution of potash, it is decomposed, yielding benzyl mercaptan, benzyl bisulphide, and a small quantity of benzoic acid. Benzal sulphide is insoluble in a solution of sodium-hydrogen sulphite.

The thiobenzaldehyde used in the following experiments was separated from benzaldehyde with which it forms an addition product, by dissolving out the latter compound with a solution of hydrogen sodium sulphite. No definite results were obtained by the action of hydrocyanic acid, or hydriodic acid on thiobenzaldehyde; but on treatment with a concentrated solution of potash, a mixture of benzyl mercaptan, benzyl bisulphide, and benzoic acid was obtained.

W. C. W.

The Hydroxytoluic Acids from the Three Isomeric Cresols, and their Oxidation to Hydroxyphthalic Acids. By C. Schall (*Deut. Chem. Ges. Ber.*, **12**, 816—836).—Reimer and Tiemann have recently (*Ber.*, **11**, 1285) proposed a method for replacing the hydrogen of the benzene ring in phenols by carboxyl, and thus converting them into hydroxy-acids. This method consists in acting on a strong alkaline solution of the sodium phenolate with carbon tetrachloride, thus:—$C_6H_4(ONa)H + CCl_4 + 5NaHO = C_6H_4(ONa).COONa + 4NaCl + 3H_2O$. Experience has shown that in reactions in which ortho- and para- compounds are simultaneously obtained, the ortho-compounds are produced in largest quantity at high temperatures, and the para-compounds at low temperatures. The author has made an application of these facts in the following investigation, by acting on the three isomeric cresols with carbon tetrachloride, and obtaining thereby the homosalicylic acids and the isomeric homoparahydroxybenzoic acids, the latter being produced in largest quantity when the reaction takes place at a comparatively low temperature (viz., 100°). The hydroxytoluic acids were then converted by oxidation into hydroxyphthalic acids, in order to determine the relations of the homosalicylic and homoparahydroxybenzoic acids on the one hand, to the hydroxyphthalic acids on the other. By treatment in this way *orthocresol* gave orthohomosalicylic acid* (m. p. 162°), and orthohomoparahydroxybenzoic acid (m. p. 172°). *Metacresol* gave metahomosalicylic acid and metahomoparahydroxybenzoic acid (177°), and another acid which probably consisted of homo-alpha-hydroxyisophthalic acid, but was not fully investigated. *Paracresol* gave only parahomosalicylic acid (m. p. 151°). The carbon tetrachloride reaction can be used

* In all cases the position of the side chain is referred to the phenolic hydroxyl.

with advantage only for the preparation of homoparahydroxybenzoic acids. The large quantities of the three homosalicylic acids required for the following investigation were, therefore, obtained by the action of carbonic anhydride on the sodium compounds of the three cresols: for, as this reaction occurs at about 200°, these ortho-compounds are obtained in far larger quantity than the para-compounds.

For the oxidation of the hydroxytoluic acids to hydroxyphthalic acids, fusion with potash could not be employed, since changes in the side-chains are liable to occur; nor could they be oxidised directly, as the benzene nucleus is then attacked, and not the methyl-group. Resort was therefore had to the methoxytoluic acids, $C_6H_3Me(OCH_3).COOH$, which, though difficult to prepare, are very stable compounds. The methylic ethers of these acids are best prepared by the action of methyl iodide on the sodium salts of the hydroxytoluic acids—

$$C_6H_5Me(ONa).COONa.$$

Methylmethorthohomosalicylate, $C_6H_3(OCH_3)(CH_3)(COOCH_3)$ = [1 : 2 : 6], is a brown oil.

Methylmethmetahomosalicylate, $C_6H_3.(OCH_3)(CH_3)(COOCH_3)$ = [3 : 1 : 4], is a thick oil.

Methylmethparahomosalicylate, $C_6H_3.(OCH_3)(CH_3)(COOCH_3)$ = [1 : 4 : 2], is also a thick oil. All these compounds have an odour resembling that of winter-green oil, and boil with partial decomposition.

Methylmethoxyorthomethylparabenzoate (methylorthohomoanissate), $C_6H_3.(OCH_3)(CH_3)(COOCH_3)$ = [1 : 2 : 4], crystallises in small plates (m. p. 67°) which are difficultly soluble in hot water, but easily soluble in alcohol, ether, benzene, and chloroform.

Methylmethoxymetamethyparabenzoate (methylmetahomoanissate), $C_6H_3.(OCH_3)(CH_3)(COOCH_3)$ = [1 : 3 : 4], is a thick oil.

The above ethers, which are all volatile in steam, were converted into the corresponding acids by heating with excess of alkali.

Methylorthohomosalicylic acid, $C_6H_3.(OCH_3)(CH_3)(COOH)$ = [1 : 2 : 6], crystallises in feathery needles (m. p. 81°).

Methylmetahomosalicylic acid, $C_6H_3.(OCH_3)(CH_3)(COOH)$ = [3 : 1 : 4], forms aggregates of needles or plates (m. p. 103°).

Methylparahomosalicylic acid, $C_6H_3.(OCH_3)(CH_3)(COOH)$ = [1 : 4 : 2], is obtained first as an oil, which gradually becomes crystalline. From dilute solutions it crystallises in long thin needles (m. p. 67°).

Methoxyorthomethylparabenzoic acid, $C_6H_3.(OCH_3)(CH_3)(COOCH)$ = [1 : 2 : 4], crystallises in minute silky needles (m. p. 192°).

Methoxymetamethylparabenzoic acid, $C_6H_3.(OCH_3)(CH_3)(COOH)$ = [1 : 3 : 4], crystallises in needles (m. p. 176°) which are more easily soluble in water than the preceding compound.

All three meth-homosalicylic acids are easily soluble in hot water, alcohol, ether, benzene, and chloroform, whilst the two parabenzoic acids are much more difficultly soluble in hot water, chloroform, and benzene, though they dissolve easily in alcohol and ether.

None of the acids give any reaction with ferric chloride. A table is given showing the reactions which the neutral and moderately con-

centrated solutions of the ammonium salts give with various reagents.

These methoxytoluic acids were converted into the corresponding methoxyphthalic acids by oxidation with potassium permanganate in alkaline solution.

β-Methoxyisophthalic acid (from methorthohomosalicylic acid), $C_6H_3.(OCH_3)(COOH)(COOH) = [1 : 2 : 6]$, crystallises in prisms (m. p. 217°), with slight decomposition and sublimation.

Methoxyterephthalic acid (from methmetahomosalicylic acid), $C_6H_3.(OCH_3)(COOH)(COOH) = [3 : 1 : 4]$, crystallises in prisms (m. p. 278°).

α-Methoxyisophthalic acid, $C_6H_3.(OCH_3)(COOH)(COOH) = [1 : 4 : 2]$, crystallises in needles (m. p. 261°). It can be obtained either from methparahomosalicylic acid or from methoxyorthomethylparabenzoic acid. The same compound has likewise been prepared by Jacobsen (*Ber.*, **11**, 898), from methyl α-metaxylenol—

$$C_6H_3.(OCH_3)(CH_3)(CH_3) = [1 : 2 : 4];$$

he, however, gives the melting point as 245°.

Methoxyorthophthalic acid (from methoxymetamethylparabenzoic acid), $C_6H_3.(OCH_3)(COOH)(COOH) = [1 : 3 : 4]$, crystallises in stellate groups of needles (m. p. 138—144°); the re-solidified mass, however, melts at 93°, owing to the formation of an anhydride, $C_9H_6O_4$, which latter is best obtained by heating the acid in a current of dry carbonic acid. It crystallises in long needles.

The aqueous solutions of the above methoxyphthalic acids give no coloration with ferric chloride, but yellow precipitates. All the acids are almost insoluble in chloroform and benzene, but easily soluble in alcohol. β-Methoxyisophthalic and methoxyorthophthalic acids are easily soluble in ether, whilst the other two are but difficultly soluble. β-Methoxyisophthalic acid is easily soluble in water, and methoxyorthophthalic acid still more easily soluble, whilst the other two are almost insoluble. A table is given showing the reactions of the four acids, with various reagents. The methoxyphthalic acids were converted into the corresponding oxyphthalic acids by heating with hydrochloric acid under pressure, and also by fusing with caustic potash. The same products were obtained in both cases.

β-Oxyisophthalic acid (from β-methoxyisophthalic acid)—

$$C_6H_3.(OH)(COOH)(COOH) = [1 : 2 : 6],$$

crystallises in long needles (m. p. 239°), which are easily soluble in hot water. The aqueous solution exhibits a slight bluish-violet fluorescence, and gives a cherry-red coloration with ferric chloride. The neutral barium salt is difficultly soluble in water. This acid has already been obtained by Tiemann and Reimer (*Ber.*, **10**, 1562) by the oxidation of orthoaldehydosalicylic acid, and by Hesse (*Ber.*, **10**, 2194) from salicylic acid by the carbon tetrachloride reaction, and by Jacobsen (*Ber.*, **11**, 902) from a β-metaxylenol $C_6H_3.(OH)(CH_3)(CH_3) = [1 : 2 : 6]$.

Oxyterephthalic acid (from methoxyterephthalic acid)—

$$C_6H_3.(OH)(COOH)(COOH) = [3 : 1 : 4],$$

does not melt at 280°. It is identical with the acid obtained by Warren de la Rue and H. Müller (*Ann. Chem. Pharm.*, **121**, 96), and also by Jacobsen (*Ber.*, **11**, 381, 571, 573), from paraxylenol thymol and carvacrol.

1.	2.	3.
Orthohomosalicylic acid, $C_6H_3^{1}.OH^{2}.CH_3^{6}.COOH$, m. p. = 164°.	Metahomosalicylic acid, $C_6H_3^{3}.OH^{1}.CH_3^{4}.COOH$ m. p. = 173°.	Orthohomomet-hydroxybenzoic acid, $C_6H_3^{2}.OH^{1}.CH_3^{4}.COOH$ m. p. = 204°.
Methorthohomosalicylic acid, $C_6H_3^{1}.OCH_3^{2}.CH_3^{6}.COOH$ m. p. = 81°.	Meth-metahomosalicylic acid, $C_6H_3^{3}.OCH_3^{1}.CH_3^{4}.COOH$ m. p. = 103°.	Methoxyortho-methylmetabenzoic acid, $C_6H_3^{2}.OCH_3^{1}.CH_3^{4}.COOH$ m. p. = 156°.
β-Methoxyisophthalic acid, $C_6H_3^{1}.OCH_3^{2}.COOH^{6}.COOH$ m. p. = 217°.	Methoxyterephthalic acid, $CH_3.OCH_3^{3}.COOH^{1}.COOH^{4}$ m. p. = 278°.	
β-Oxyisophthalic acid, $C_6H_3^{1}.OH^{2}.COOH^{6}.COOH$ m. p. = 239°.	Oxyterephthalic acid, $C_6H_3.OH^{3}.COOH^{1}.COOH^{4}$ m. p. above 300°.	

4.	5.	6.
Parahomosalicylic acid, $C_6H_3^{1}.OH^{4}.CH_3^{2}.COOH$ m. p. = 151°.	Orthohomoparahydroxybenzoic acid, $C_6H_3^{1}.OH^{2}.CH_3^{4}.COOH$ m. p. = 172°.	Metahomoparahydroxybenzoic acid, $C_6H_3^{1}.OH^{3}.CH_3^{4}.COOH$ m. p. = 178°.
Methparahomosalicylic acid, $C_6H_3^{1}.OCH_3^{4}.CH_3^{2}.COOH$ m. p. = 67°.	Methoxyorthomethylparabenzoic acid, $C_6H_3^{1}.OCH_3^{2}.CH_3^{4}.COOH$ m. p. = 192°.	Methoxymetamethylparabenzoic acid, $C_6H_3^{1}.OCH_3^{3}.CH_3^{4}.COOH$ m. p. = 176°.
α-Methoxyisophthalic acid, $C_6H_3^{1}.OCH_3^{4}.COOH^{2}.COOH$ m. p. = 261°.		Methoxyorthophthalic acid, $C_6H_3^{1}.OCH_3^{3}.COOH^{4}.COOH$ m. p. = 138—144°.
α-Oxyisophthalic acid, $C_6H_3^{1}.OH^{4}.COOH^{2}.COOH$ m. p. above 300°.		Oxyorthophthalic acid, $C_6H_3^{1}.OH^{3}.COOH^{4}.COOH$ m. p. = 181°.

α-Oxyisophthalic acid (from α-methoxyisophthalic acid)—

$$C_6H_3.(OH)(COOH)(COOH) = [1:2:4]$$

(m. p. 306° uncorr.), is identical with the acid obtained by Ost (*J. pr. Chem.*, *N.F.*, **14**, 103); Tiemann and Reimer (*Ber.*, **10**, 1571—1572); Jacobsen (*Ber.*, **11**, 374, 898), &c.

Oxyorthophthalic acid (from methoxyorthophthalic acid)—

$$C_6H_3.(OH)(COOH)(COOH) = [1:3:4]$$

(m. p. 181°). Identical with the acid obtained by Baeyer (*Ber.*, **10**, 1079) from amidophthalic acid.

The table (p. 794) exhibits the relations of all the compounds referred to above. T. C.

Derivatives of Hydroxypropylbenzoic Acid. By R. Meyer (*Deut. Chem. Ges. Ber.*, **12**, 1071—1076).—When hydroxypropylbenzoic acid is treated with a mixture of potassium dichromate and dilute sulphuric acid, an energetic reaction takes place, carbonic anhydride is evolved, and a white powder separates out which consists of a mixture of terephthalic acid and an acid having the composition $C_9H_8O_3$, probably para-acetylbenzoic acid, or acetophenone-carbonic acid, $CH_3.CO.C_6H_4.COOH$. The acids are separated by recrystallising their ammonium salts. The new acid is sparingly soluble in alcohol, ether, and cold water. From hot water it is deposited in glistening white needles, which melt at 200°, and sublime at a higher temperature. The methyl salt is more soluble in alcohol than methyl terephthalate.

It is deposited on cooling from a hot aqueous solution in white needles, which melt at 92° and sublime below 100°. A partial decomposition takes place on saponification, a small quantity of terephthalic acid being formed.

The *methyl* salt of the polymeric modification of propenylbenzoic acid (*Ber.*, **11**, 2172) melts at 83°, but decomposes on distillation. The acid chloride and the ethyl salt also decompose on boiling. The ammonium, calcium, and copper salts of this acid are crystalline. The acid is converted into cumic acid by the action of hydriodic acid and amorphous phosphorus. W. C. W.

Benzyl-methylglycollic Acid. By S. Gabriel and A. Michael (*Deut. Chem. Ges. Ber.*, **12**, 814—816).—*Benzyl-methylglycollic acid*, $CMe(C_7H_7)(OH).COOH$, is best obtained by digesting the sodium hyposulphite compound of phenylacetone with a mixture of 1 part potassium cyanide, 1 part water, and 10 parts alcohol in closed vessels at 100°. It crystallises in brilliant prisms (m. p. 98°), which become dull on exposure. It is readily soluble in warm water and in alcohol, and also in alkalis. On warming with concentrated sulphuric acid, it splits up into carbon monoxide and phenylacetone,—

$$C(C_7H_7)(CH_3)(OH).COOH = CO + H_2O + C_7H_7.CO.CH_3.$$

T. C.

Acids produced by the Introduction of Chloro- and Bromobenzene into the Animal System. By M. JAFFE (*Deut. Chem. Ges. Ber.*, **12**, 1092—1098).—An acid having the composition $C_{21}H_{22}N_2Br_2S_2O_5$ or $C_{11}H_{12}NBrSO_3$, can be obtained by subjecting the urine of a dog (to which bromobenzene has been administered) to the following treatment. The urine is evaporated to dryness, and the residue extracted with alcohol. After distilling off the alcohol, the residue is acidified with dilute sulphuric acid and treated with ether. On evaporation the ethereal extract leaves a syrupy liquid, which crystallises on the addition of water. The acid is purified by shaking up its ammonium salt with ether, which removes most of the impurities. Hydrochloric acid is then added to the ammonium salt, when the acid separates out in colourless needles or prisms, soluble in hot dilute acetic acid or hot dilute alcohol. This substance melts at 152°, and decomposes at a high temperature. The barium salt, $C_{21}H_{20}N_2BrS_2O_5Ba$ or $(C_{11}H_{10}NBrSO_3)_2Ba$, is a sparingly soluble crystalline compound.

The acid is decomposed by boiling with dilute hydrochloric acid, needle-shaped crystals of a hydrochloride separating out. From this salt the free base, $C_9H_{10}BrSNO_2$, may be obtained by precipitation with ammonium acetate. It crystallises in needles or scales (m. p. 180—184°), which are insoluble in water and ether, but dissolve freely in mineral acids.

By a process similar to the above, the compound $C_{21}H_{22}N_2Cl_2S_2O_5$, or $C_{11}H_{12}NClSO_3$, m. p. 153°, can be obtained from the urine of a dog which has taken doses of monochlorobenzene. This body is deposited from an aqueous or alcoholic solution in colourless plates, and from an ethereal solution in thin transparent rhombic tables. It is decomposed by boiling with hydrochloric acid, yielding a base $C_9H_{10}ClNSO_2$, which crystallises in needles or plates (m. p. 182—184°) soluble in hot water and in alcohol.

The author considers that these experiments confirm the results of Baumann and Preusse (*Zeits. f. Physiol. Chem.*, **3**, pt. 1).

W. C. W.

Nitro-, Amido-, and Bromo-benzenesulphonic Acids. By L. SPIEGELBERG (*Liebig's Annalen*, **197**, 257—306).—*Parabromobenzenesulphonic acid* was prepared according to Gorlich's method (*Annalen*, **180**, 95), the author observing the simultaneous formation of dibromosulphobenzide, in small quantity; this acid yielded, on boiling with nitric acid, in addition to *nitroparabromobenzene-sulphonic acid*, a mixture of nitrobromobenzene [1 : 4] and dinitrobromobenzene, $NO_2 : NO_2 : Br = [1 : 3 : 4]$; the former of these was obtained in small white needles (m. p. 127°), the latter in yellowish prisms (m. p. 71·5°), from the alcoholic solution of the mixture. This dinitrobromobenzene crystallises from its solution in benzene in transparent plates, which retain one half mol. benzene, and melt at 65°. The reduction of the nitro-acid was effected by treatment with a solution of stannous chloride; the resulting *amidobromobenzenesulphonic acid*,

$$SO_3H : NH_2 : Br = [1 : 3 : 4],$$

crystallises from a concentrated solution in anhydrous, long white

needles; these when allowed to remain for some days in contact with the solution, are converted into well-formed yellowish prisms containing 1 mol. H_2O. The acid is freely soluble in hot water, slightly soluble in cold, still less soluble in alcohol. Its salts are characteristic; their composition is expressed by the general formula,

$$C_6H_3(NH_2)Br.SO_3M'.nH_2O.$$

The following are described:—The *potassium salt* ($1H_2O$) forms rhombic plates of a reddish colour, freely soluble in water. The *barium salt* ($1H_2O$) is obtained in well-formed prisms, which are easily soluble in water and in dilute alcohol, forming colourless solutions, which develope a reddish tint on standing. The *calcium salt* ($2H_2O$) crystallises slowly from its concentrated aqueous solution in large four-sided plates of a reddish-yellow colour. The *lead salt* (anhydrous) forms bright red rhombic prisms. The *silver salt* ($1{\cdot}5H_2O$) is obtained in rhombic prisms of a brown colour.

The acid thus described is identical with that which Langfurth obtained (*Annalen*, **191**, 176) by brominating metamidobenzenesulphonic acid.

Dibromobenzenesulphonic acid, $SO_3H:Br:Br = [1:3:4]$, was obtained from the preceding compound by means of the diazo-reaction, in the form of slender white needles (m. p. 68°), containing 3 mols. H_2O. After dehydration at 130° the acid melts at 67°. Goslich, on the other hand, gives 57—58° as the melting point of the acid (with 3 mols. H_2O), and states (*loc. cit.*) that the dehydrated acid is so hygroscopic that a determination of its melting point was impossible. To remove all doubt on this point, the author prepared a specimen of the acid from the silver salt of parabromobenzenesulphonic acid, and found that its melting point was identical with the above; also that the dehydrated acid was not hygroscopic. In explanation of these contradictory results, the author suggests the possible presence of sulphuric acid in Goslich's preparation, which was obtained by the decomposition of the barium salt by sulphuric acid. The lead salt, $(C_6H_3Br_2.SO_3)_2Pb.2H_2O$, crystallises in concentric groups of white needles. The following data indicate the solubility of the salt in water: 100 grams of the solution contained—

	Gram.	
After 1 day at 15°	0·432	of the anhydrous salt
„ 3 days at 11°	0·391	„ „
„ 8 days at 1°	0·333	„ „

The barium salt, $(C_6H_3Br_2.SO_3)_2Ba.2H_2O$, crystallises in white shining plates: 100 grams of its aqueous solution contained—

	Gram.	
After 6 hours at 11°	0·380	of the anhydrous salt
„ 2 days at 1°	0·254	„ „

Dibromobenzenesulphochloride, $C_6H_3Br_2.SO_2Cl$, was obtained by the action of phosphorus pentachloride on the potassium salt: it crystallises from its ethereal solution in white needles (m. p. 34°). The corresponding sulphamide obtained by the action of ammonia on the

chloride, crystallises in slender colourless needles (m. p. 175°), which are slightly soluble in water.

Amido-dibromobenzenesulphonic acid, $SO_3H : NH_2 : Br : Br = [1:3:4:6]$ is separated on the addition of bromine (1 mol.) to the aqueous solution of the monobromo-acid.

It is remarkable that the reduction of the nitromonobromobenzenesulphonic acid to the amido-acid previously described, is accompanied by the formation of this dibromo-acid in some quantity. Although this does not appear to be due to the presence of dibromobenzene in the monobromobenzene from which the sulphonic acid was prepared, the author has not finally satisfied himself that no similar disturbing cause contributed to the result.

The product is identical with the acid previously described by Berndsen, Beckurts, and others (*Annalen*, **177**, 84, 181, 213, &c.). The determination of its solubility in water gave the following results: 100 grams of the solution contained:—

	Gram.
After 4 hours at 24°	0·3696 of the acid
„ 2 days at 22°	0·3210 „
„ 5 days at 22°	0·3039 „

The potassium salt, $C_6H_2.(NH_2)Br_2.SO_3KH_2O$, crystallises in rhombic tables of a reddish colour, which are somewhat soluble in water. The barium salt crystallises with $6H_2O$ in long needles of a reddish colour, which are easily soluble in water: the solution developes a deep red colour on evaporation. The lead salt crystallises in tables (anhydrous) of a red colour. The acid is decomposed on heating with concentrated hydrochloric acid at 250°, with formation of sulphuric acid and a mixture of bromine derivatives of benzene and aniline; with water at the same temperature, the decomposition takes a different direction, a small quantity only of sulphuric acid, as also of volatile bromine compounds, being formed, but in place of them amidobromobenzenesulphonic acid and metamidobenzenesulphonic acid.

Dibromobenzenesulphonic acid, $SO_3H : Br : Br = [1:4:6]$, was obtained from the preceding acid by means of the diazo-reaction. It is identical with that prepared by Bässmann (*Annalen*, **191**, 229) from metamidobenzenesulphonic acid (the starting point of the author's investigation was parabromobenzenesulphonic acid).

Tribromobenzenesulphonic acid, $SO_3H : Br_3 = [1:3:4:6]$, was prepared from amidodibromobenzenesulphonic acid by Langfurth's method (*Annalen*, **181**, 188). It crystallises from its aqueous solution with $3H_2O$ in white needles; after dehydration the acid melts at 140°. The author corroborates Langfurth as regards the formation of (1:2:4) tribromobenzene by heating this acid with hydrobromic acid at 200°. The potassium salt, $C_6H_2Br_3.SO_3K.H_2O$, crystallises in long white silky needles, which are easily soluble in hot water; the solution saturated at 22° contains about 0·8 per cent. of the anhydrous salt. The barium salt is obtained as a bulky precipitate, which speedily becomes crystalline, the crystals having the form of rhombic plates, and containing 3 mols. H_2O. The aqueous solution saturated at 22° contains about 0·1 per cent. of the anhydrous salt.

Tribromobenzenesulphochloride, $C_6H_2Br_3.SO_2Cl$, crystallises in transparent rhombic prisms (m. p. 85·5°), which are freely soluble in ether. The corresponding amide crystallises in microscopic needles (m. p. 223°), which are only sparingly soluble in hot water.

Amidotribromobenzenesulphonic acid, $SO_3H : Br : NH_2 : Br_2 = [1:2:3:4:6]$, is formed, simultaneously with the dibromo-acid, on adding bromine (1 mol.) to the aqueous solution of the amido monobromo-acid. The properties of the acid thus obtained identify it with that formulated as above, by Langfurth and Bässmann and others. The following table sets forth the author's data respecting the acid and its salts:—

	H_2O crystallisation.	In 100 grams sat. solution.
Free acid	1 mol.	11 grams at 13°
Ammonium salt	1 „	6 „ „ 14
Potassium „	1 „	1 „ „ 16
Barium „	9 mols.	0·75 „ „ 25
Lead „	9 „	0·75 „ „ 15

The decomposition of this acid on heating it with water, with formation of the dibromo-acid, is represented by the equation:

$$C_6HBr_3(NH_2)SO_3H + H_2O = C_6H_2Br_2(NH_2)SO_3H + HBr + O.$$

The author investigated this reaction in relation to the further action of the O-atom, thus supposed to be liberated. He obtained, in addition to the dibromo-acid, a quantity of carbonic anhydride, ammonia, sulphuric acid, and apparently also bromoform and tribromaniline. A portion of the acid appears therefore to undergo complete oxidation.

The author, having thus investigated the relation of amidobromobenzenesulphonic acid to bromine, and the structure of the acids resulting from the reaction of these bodies, proceeds, in the second part of this paper, to the results of the study of the derivatives of the acid formed by the action of bromine on the silver salt of parabromobenzenesulphonic acid. This acid has been shown by Goslich (*Annalen*, **186**, 148) to be a dibromobenzenesulphonic acid of the structure, $SO_3H : Br : Br : = [1:3:4]$. On nitrating this acid he obtained a nitro-compound, which he did not further investigate. This the author finds to yield on reduction the *Amidodibromobenzenesulphonic acid*, $SO_3H : Br_2 : NH_2 = [1:3:4:6]$. In the pure state the acid crystallises (anhydrous) in rhombic plates, which are only slightly soluble in water, and almost insoluble in alcohol. It resists the action of water at 175°; on heating with hydrochloric acid at 160°, it appears to yield a dibromaniline (m. p. 80°).

The following table contains the author's data concerning the acid and its salts:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Free acid.....	Rhombic plates.	Anhydrous.	0·15 at 26°.
Ammonium salt..	Rhombic plates (rose-coloured).	1 mol.	Freely soluble.
Potassium „ ..	Thin plates.	2 mols.	Freely soluble at 100°.
Barium „ ..	Rhombic plates.	1 mol.	0·65 at 14°.
Calcium „ ..	Needles (yellowish).	3 mols.	Easily soluble.
	Rhombic prisms.	4 mols.	
Lead „ ..	Long prisms.	1 mol.	0·16 at 14°.
Silver „ ..	Small plates (brown).	Anhydrous.	0·05 at 15°.

On heating this acid with potassium nitrite and hydrobromic acid in presence of glacial acetic acid, *tribromobenzenesulphonic acid*, $SO_3H : Br_3 = [1:3:4:6]$, was obtained identical in every respect with that described in the first part. This acid yielded on nitration *nitrotribromobenzenesulphonic acid*, $SO_3H : Br_2 : NO_2 : Br = [1:3:4:5:6]$, together with *nitrotribromobenzene*, $NO_2 : Br_3 = [1:3:4:6]$. The following is a tabular statement of the author's data respecting the former compound:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Free acid.....	Rhombic prisms.	3 mols.	Easily soluble.
Ammonium salt..	Long needles.	Anhydrous.	1·77 at 9°.
Potassium „ ..	Plates.	Anhydrous.	1·32 at 10°.
Barium „ ..	Needles.	3 mols.	0·70 at 10°.
Calcium „ ..	Plates.	4·5 mols.	1·95 at 9°.
Lead „ ..	Long prisms.	6 mols.	0·88 at 6°.
Silver „ ..	Prisms.	1 mol.	0·45 at 6°.

Nitrotribromobenzenesulphochloride, $C_6H(NO_2)Br_3.SO_2Cl$, crystallises in small shining plates (m. p. 143°); the corresponding amide in small pearly plates (m. p. about 260°).

Amidotribromobenzenesulphonic acid, $SO_3H : Br_2 : NH_2 : Br = [1:3:4:5:6]$, obtained by reduction from the nitro-acid, crystallises in long white prisms (with 1·5 mol. H_2O), or in slender white needles (with 1 mol. H_2O). On heating with water at 195°, it yields the corresponding dibromo-acid; no sulphuric acid nor volatile compounds appear to be formed.

The following are the properties of its salts:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Ammonium salt..	Small prisms.	Anhydrous.	Easily soluble.
Potassium „ ..	Rhombic prisms.	1 mol.	2·25 at 4°.
Barium „ ..	Small plates.	Anhydrous.	0·09 at 4°.
Calcium „ ..	Radiating prisms.	3·5 mols.	Easily soluble.
Lead „ ..	Long needles.	2 mols.	0·44 at 3°.
Silver „ ..	Microscopic needles.	0·5 mol.	0·56 at 11°.

The *diazo-compound*, $C_6H.Br_3\begin{matrix}N\\SO_3\end{matrix}\rangle\!\rangle N$, is precipitated in the form of yellowish needles on passing nitrous acid into the aqueous or alcoholic solution of the amido-acid. It is dissolved by boiling hydrobromic acid with formation of *tetrabromobenzenesulphonic acid*, $SO_3H : Br_4 = [1:3:4:5:6]$. This acid crystallises (with 2 mols. H_2O) in white shining plates. It is dehydrated at 120°, melts at 168—169°, and at a higher temperature is decomposed with evolution of white fumes. The following table exhibits the characteristics of its salts:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Ammonium salt..	Microscopic needles.	Anhydrous.	1·2 at 11°.
Potassium „ ..	Rhombic tables.	1 mol.	0·19 at 11°.
Barium „ ..	Microscopic prisms (rhombic).	1 mol.	0·02 at 10·5°.
Calcium „ ..	Microscopic tables (rhombic).	3 mols.	0·2 at 11°.
Lead „ ..	Slender needles.	3 mols.	0·05 at 11·5°.
Silver „ ..	Concentric needles.	1 mol.	0·17 at 11°.
	„ plates.	0·5 mol.	

Tetrabromobenzenesulphochloride, $C_6HBr_4.SO_2Cl$, crystallises from ether in shining white plates; from benzene in rhombic prisms (m. p. 120°): the corresponding amido-compound crystallises from alcohol in yellowish prisms.

The comparison of the above compounds with those of the three known isomeric forms of tetrabromobenzenesulphonic acid, together with the origin of the acid, identify it, beyond doubt, with that described by Lenz (*Annalen*, **181**, 23).

Nitro-tetrabromobenzenesulphonic acid, $SO_3H : NO_2 : Br_4 = [1:2:3:4:5:6]$, is formed, together with nitro- (or dinitro-) tetrabromobenzene, on treating the above acid with concentrated nitric acid. It crystallises with 1 mol. H_2O in slender needles, which are freely soluble in water, alcohol, and ether; it is dehydrated at 126°, and melts at 171—173°. The characteristics of its salts are the following:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Ammonium salt..	Long needles.	Anhydrous.	0·5 at 11°.
Potassium „ ..	4-sided plates.	1 mol.	0·2 at 11°.
Barium „ ..	Prisms from concentrated solution.	4 mols.	0·19 at 10°.
	Needles.	9 mols.	
Calcium „ ..	Slender needles.	1 mol.	3·55 at 10°.
Lead „ ..	Microscopic plates.	2 mols.	0·037 at 10°.

Nitro-tetrabromobenzenesulphochloride, $C_6Br_4(NO_2).SO_2Cl$, crystallises from its ethereal solution in white prisms (m. p. 173°), the corresponding amide, in microscopic plates, which are freely soluble in alcohol, but with difficulty in water.

Amido-tetrabromobenzenesulphonic acid, $SO_3H : NH_2 : Br_4 = [1:2:3:4:5:6]$, obtained by reduction from the preceding nitro-acid, crystallises with 2 mol. H_2O in needles. It is dehydrated at 125°, and undergoes decomposition at 130°. It is decomposed on heating with water at 135°, with formation of bromanilines and sulphuric acid. The acid is freely soluble in alcohol; 100 grams of the saturated aqueous solution (at 13°) contains 0·028 gram of the anhydrous acid. Its salts present the following characteristics:—

	Crystalline form.	H_2O crystallisation.	In 100 grams saturated solution.
Potassium salt...	4-sided plates.	1 mol.	0·12 at 13°.
Barium „ ...	Microscopic needles.	1 mol.	0·015 at 11°.
Calcium „ ...	Needles and plates.	2 mols.	0·12 at 13°.

The *diazo-compound*, $C_6Br_4\langle\begin{matrix}N\\SO_3\end{matrix}\rangle N$, is precipitated as a yellow crystalline powder on passing nitrous acid into the alcoholic solution of the preceding amido-acid. On heating it with concentrated hydrobromic acid, *pentabromobenzenesulphonic acid* is formed.

C. F. C.

Pentabromobenzene-sulphonic Acid. By Heinzelmann and L. Spiegelberg (*Liebig's Annalen*, **197**, 306—320).—The pentabromo-acid, $C_6Br_5.HSO_3$, prepared by the authors as described in the preceding paper, and also its compounds, exhibited properties differing considerably from those observed by Beckurts and Langfurth for the same bodies (*Annalen*, **181**, 226, and **191**, 208). Thus the authors find that the free acid is easily soluble in water, whereas the latter chemists state that it is difficultly soluble. A considerable discrepancy further occurs between the observed solubilities of the potassium and barium salts, as also between the numbers given for the melting point of the chloride, 153—154° as against 90° and 97°. Having by close investi-

gation satisfied themselves of the purity of the acid prepared as above, they have repeated the latter stages of the method adopted by Beckurts and Langfurth, starting from the amidotribromo-acid,

$$(SO_3H : Br : NH_2 : Br_2 = 1 : 2 : 3 : 4 : 6),$$

and found in one case that in place of the pentabromo-acid they obtained the tetrabromo-acid, and in a second, in which special precautions were taken to ensure the purity of the barium nitro-tetrabromobenzenesulphonate—the penultimate stage in the preparation—they obtained a purer product, but still mixed with the tetrabromo-acid. The discrepancies above mentioned must therefore be referred to the admixture of the tetrabromo- with the pentabromo-acid investigated by Beckurts and Langfurth.

Potassium Pentabromobenzenesulphonate, $C_6Br_5KSO_3$, crystallises in plates and needles, which are only sparingly soluble in water, containing potassium carbonate. The *barium* salt, $(C_6Br_5.SO_3)_2Ba.H_2O$, forms sparingly soluble microscopic six-sided plates belonging to the rhombic system. The *chloride*, $C_6Br_5.SO_2Cl$, forms rhombic prisms (m. p. 153—154°), sparingly soluble in ether. The *amide*, $C_6Br_5.SO_2NH_2$, obtained by the action of ammonia on the chloride, crystallises in nodules, which become brown and sinter slightly at 245°, but do not melt even at 290°. It is decomposed at a higher temperature.

C. F. C.

Bromophenyl-mercapturic Acid. By E. Baumann and C. Preusse (*Deut. Chem. Ges. Ber.*, **12**, 806—810).—A continuation of the authors' previous work (*Pflüger's Arch.*, **13**, 291) on the action of the animal system on benzene and phenol. An examination of the urine of a dog, to which 3 to 4 grams of bromobenzene had been daily administered for six months, showed:—(1.) That the proportion of sulphates had diminished, and that the urine contained large quantities of bromophenolsulphonic acid, which yielded parabromophenol when boiled with hydrochloric acid. (2.) Ether extracts small quantities of pyrocatechol from the urine, after the latter has been warmed with hydrochloric acid. (3.) The fresh urine turns the plane of polarisation strongly to the left, and reduces cupric oxide in alkaline solution. The optical substance present was easily decomposed by acids and alkalis, and was not precipitated by lead acetate. (4.) The urine contains *bromophenyl-mercapturic acid*, $C_{11}H_{10}BrNSO_3$ (m. p. 152°). This acid is readily soluble in alcohol, but almost insoluble in ether and cold water; it dissolves in 70 parts of boiling water. It is a monobasic acid, the alkaline salts of which are easily soluble; those with alkaline-earths difficulty soluble, and those with the heavy metals insoluble. The *barium salt*, $(C_{11}H_9BrNSO_3)_2Ba + 2H_2O$, loses its water of crystallisation at 100°. Bromophenyl-mercapturic acid when boiled with alkalis splits up into ammonia, acetic acid, and bromophenyl mercaptan, C_6H_5BrS (m. p. 74°) (Hübner and Alsberg, *Annalen*, **156**, 308). On boiling with Fehling's solution it gives a yellow precipitate of the copper-compound of the mercaptan, which reaction may be used for the recognition of the original acid. Boiling concentrated hydrochloric acid or dilute sulphuric acid (1 to 4) decomposes bromophenyl-mercapturic acid, forming acetic acid and a substance,

$C_9H_8BrSNO_2$, of feeble basic properties. It is almost insoluble in water, and crystallises from boiling alcohol in needles (m. p. 181° with decomposition). The following represents its formation: $C_{11}H_{10}BrSNO_3 + H_2O = C_9H_8BrSNO_2 + C_2H_4O_2$. On boiling with alkalis it gives the same products as bromophenyl-mercapturic acid.

T. C.

Liquid Toluenesulphonic Chloride, and Beckurts' so-called Toluenemetasulphonic Acid. By C. Fahlberg (*Deut. Chem. Ges. Ber.*, **12**, 1048—1052).—When liquid toluenesulphonic chloride is treated with aqueous ammonia a mixture of tolueneorthosulphamide and Beckurts' toluenemetasulphamide (*Ber.*, **10**, 943) separates out, leaving in the mother-liquor a toluenedisulphamide (m. p. 187°), which is identical with that obtained by Blomstrand (*Ber.*, **5**, 1084).

Beckurts' toluenemetasulphamide can be separated from the orthosulphamide by the greater solubility of the former in water. On oxidation with potassium permanganate, parasulphaminebenzoic, anhydro-orthosulphaminebenzoic- and orthosulphobenzoic acids are formed. This shows that the so-called metasulphamide is in reality a mixture of ortho- and para- toluenesulphamides.

Toluenedisulphonic acid can easily be prepared by heating toluenemonosulphonic chloride with strong sulphuric acid. The amide derived from this acid melts at 187°. W. C. W.

Aromatic Thiocarbamides. By B. Rathke (*Deut. Chem. Ges. Ber.*, **12**, 772—774).—Mono- and di-phenylthiocarbamide, and also phenylxanthamide, CS.(OEt)NH.PH, are soluble in caustic soda or potash, but are reprecipitated unchanged on the addition of an acid, whereas phenylthiocarbimide is insoluble in alkalis. The author explains these facts by supposing that the hydrogen in the radicle (NH.PH) is replaced by the metal of the alkali; as this hydrogen is wanting in the thiocarbimide the latter is insoluble in alkali.

The solubility of the above compounds in aqueous alkalis serves as a very ready means of separating them from other bodies, and especially where it is required to substitute oxygen for sulphur in a thiocarbamide by means of lead oxide. This oxide being also soluble in caustic alkali, the reaction takes place much more readily than when an alcoholic solution is employed. This process has been applied with great advantage in the proportion of diphenylguanidine from the corresponding thiocarbamide, and also in that of *phenylcyanamide* from monophenylthiocarbamide. The phenyl-cyanamide remains dissolved in the alkali, and on addition of acetic acid is precipitated as the hydrate in colourless plates, which melt on exposure over sulphuric acid, owing to loss of water and formation of the syrupy anhydrous phenylcyanamide. This anhydrous compound rapidly absorbs water on exposure to the air, and is again converted into the crystalline hydrate. This explains Hofmann's (*Ber.*, **3**, 267) observation that the alcoholic solution of phenylcyanamide yields a syrupy mass on evaporation. T. C.

Action of Phenyl-thiocarbimide on Diphenyl-guanidine. By B. Rathke (*Deut. Chem. Ges. Ber.*, **12**, 774—776).—A new base, which is a substitution-product of thio-dicyandiamine, is obtained

by the direct combination of phenyl-thiocarbimide and diphenyl-guanidine both dissolved in benzene. The mixture is left in the cold for about a week with frequent shaking, thus: $NPH : CS + NH : C(NHPh)_2 = NHPh.CS.NPh.C(NHPh) : NH$. The new base (m. p. 150°) is white; it is but little soluble in benzene, very difficultly soluble in alcohol, but easily in chloroform, to which it imparts a yellowish-green colour. The hydrochloride is more soluble in alcohol than the free base, and is decomposed into free acid and base by a large excess of water. On heating with a silver salt, its sulphur is precipitated as sulphide of silver.

If, however, phenyl-thiocarbimide is *heated* with diphenyl-guanidine (or better if the above addition-product itself be heated to 140°) a different reaction occurs, the products of which appear to consist in great part of a mixture of diphenyl-thiocarbamide, and the thiocyanates of two bases. One of these latter contains sulphur, and forms a hydrochloride which is almost insoluble in water and alcohol, and the ammoniacal solution of which gives with silver nitrate a lemon-yellow precipitate remaining unchanged on boiling. The other contains no sulphur, melts below 100°, and is soluble in alcohol in all proportions; it dissolves also in acids.

When the hydrochloride of the base obtained by the action of phenyl-thiocarbimide on diphenyl-guanidine in the cold is heated for some hours at 140°, diphenyl-guanidine alone remains, whilst phenyl-thiocarbimide volatilises. It was not found possible to get triphenyl-guanidine and phenyl-thiocarbimide to enter into combination.

T. C.

Action of Phosphorus Pentachloride on Thiocarbimides. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, **12**, 1126—1130).—By the action of phosphorus pentachloride on phenylthiocarbimide at 160° isocyanophenylchloride and chlorophenylthiocarbimide are formed, thus: $C_7H_5NS + PCl_5 = C_7H_5NCl_2 + PCl_3S$, and $C_7H_5NS + PCl_5 = C_7H_4ClNS.HCl + PCl_3$.

The *chlorophenylthiocarbimide* hydrochloride separates out in the crystalline form; the mother-liquor on distillation yields phosphorus trichloride, phosphorus thiotrichloride, isocyanophenylchloride (b. p. 212°), and a higher boiling product containing chlorophenylthiocarmide (b. p. 245°).

The hydrochloride is soluble in alcohol, absolute ether, chloroform, and benzene. It is rapidly decomposed by water, forming chlorophenylthiocarbimide, C_7H_4ClNS, which separates out as a heavy oil (b. p. 248°). This substance does not possess any of the characteristic properties of a substituted thiocarbimide. It is not attacked by alcohol or by ammonia at 100°, but is split up by the action of water at a high temperature, yielding hydroxyphenylthiocarbimide and hydrochloric acid.

Hydroxyphenylthiocarbimide, $C_7H_4(OH)NS$, is most conveniently prepared by boiling crude chlorophenylthiocarbimide hydrochloride with alcohol until the separation of an oily liquid no longer takes place on the addition of dilute alkali. On the addition of hydrochloric acid, an oil separates out, which after some time solidifies to a crys-

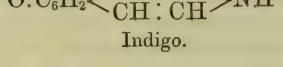
talline mass (m. p. 136°). The crystals dissolve in ether, and in solutions of potash and soda.

Amidothiocarbimide, $C_7H_4(NH_2)NS$, is formed by the action of alcoholic ammonia on chlorophenylthiocarbimide at 160°. It is a crystalline compound soluble in alcohol, and acts as a weak base.

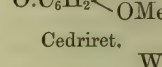
Anilidothiocarbimide, $C_7H_4(NHC_6H_4)NS$, is obtained in colourless needles (m. p. 157°) when alcoholic ammonia is replaced by aniline in the preceding experiment. This body also appears to be formed by the action of phosphorus pentachloride on diphenylthiocarbamide.

W. C. W.

Constitution of Indigo. By E. Baumann and F. Tiemann (*Deut. Chem. Ges. Ber.*, **12**, 1098—1104).—The indican found in the urine of animals which have had indole administered to them is indoxylsulphuric acid. The chemical properties of this compound and its formation in the animal system show that it bears a strong resemblance to the phenolsulphuric acids. The potassium salt is decomposed by dilute hydrochloric acid, forming *indoxyl*, an isomeride of oxindole, $C_8H_6NSO_4K + H_2O = HKSO_4 + C_8H_6N(OH)$. The constitution of indoxyl may be represented as $C_6H_3COH<\overset{CH:CH}{\underline{\qquad}}>NH$. Indoxyl can easily be converted into indigo; for instance, indigo sublimes when potassium indoxylsulphate is heated. It also separates out in the crystalline state on the addition of hydrochloric acid to a mixture of potassium indoxylsulphate and ferric chloride, or any other weak oxidising agent: $2C_8H_6N(OH) + O_2 = C_{16}H_{10}N_2O_2 + 2H_2O$. This reaction is analogous to that which takes place when ethylic dimethylpyrogallate is converted into cedriret by the action of ferric chloride, $2(C_8H_9O_2.OH) + O_2 = C_{16}H_{16}O_6 + 2H_2O$. Liebermann has shown (*Ber.*, **5**, 746, and **6**, 381) that cedriret is a derivative of diphenyl-quinone: hence the authors conclude that indigo is also a diphenyl-quinone derivative, having the following constitution:—



Indigo.



Cedriret.

W. C. W.

Aromatic Products of the Putrefaction of Albumin. By L. Brieger (*Deut. Chem. Ges. Ber.*, **12**, 705—706).—During putrefaction of albumin (hors-eliver) with cloacal matter, phenol is formed after 24 hours, whilst with pancreas it does not appear until the fifth or sixth day. Horse-liver, mixed with twice its weight of water and some pancreas after putrefaction for 5—6 days, the reaction being kept faintly alkaline, yielded a considerable amount of indole. The formation of indole is promoted by keeping the mass at a temperature of 40°. Phenol is formed abundantly at ordinary temperatures. Both these bodies are formed more slowly when air is excluded. When the putrefaction goes on for a long time, traces only of indole are obtained, but an oily liquid with a nauseous odour is formed, which is converted in the animal body into indican, and seems therefore to be

allied to indole. Traces of phenol and indole have been detected in the excrements of horses and cows, and in the lower part of the rectum, but were not found in the remaining part of the intestines, owing, no doubt, to re-absorption from the more liquid contents of the intestinal canal.

A fatty liquid—probably caproic acid—is contained in the excrements of the horse; while in those of the cow only lower fatty acids are present. G. T. A.

Oxidation of Bromonaphthalene. By Beilstein and Kurbatoff (*Deut. Chem. Ges. Ber.*, **12**, 698).—The chief product is phthalic acid. In addition, a resinous body containing bromine, and an acid also containing bromine (bromophthalic acid?) were obtained.

G. T. A.

Absorption-spectrum of Alizarin and of some Colouring Matters derived from it. By A. Rosenstiehl (*Compt. rend.*, **88**, 1194—1196).—The spectra were obtained with aqueous solutions of the sodium salts of the different substances. Alizarin gives three bands, which, if the thickness of the layer be increased, widen until they form a continuous absorption-band from C to F, with three maxima near C, D, and E. The substitution of NO_2 or OH for hydrogen in the alizarin, giving respectively nitroalizarin and purpurin, causes the disappearance of the absorption at C, and of that between D and E. Pseudo-purpurin, *i.e.*, purpurin in which COOH has been substituted for hydrogen, gives only continuous absorption in the green. As a general rule, substitution in the molecule of alizarin tends to efface the details of its spectrum. The author also finds that the greater the thickness of the layer of the solution of the colouring matter, the redder is its colour, owing to the increased absorption of the violet end of the spectrum. C. H. B.

Synthesis of Chrysene. By C. Graebe and H. Bungener (*Deut. Chem. Ges. Ber.*, **12**, 1078—1079).—The authors have obtained chrysene by the reduction of benzyl-naphthyl ketone, $C_6H_5.CH_2.CO.C_{10}H_7$. In order to prepare the ketone, a mixture of the chlorides of phenylacetic acid and of naphthalene was treated with aluminium chloride, and the product was washed with water and extracted with ether. By recrystallising from alcohol the residue which remained on evaporating the ethereal solution, benzyl-naphthyl ketone was obtained in tabular crystals, which melt at 57°.

The hydrocarbon, $C_6H_5.CH_2.CH_2.C_{10}H_7$, was not obtained in a state of purity by the action of hydriodic acid and phosphorus at 160° on the ketone. On passing the crude mixture through a red-hot tube, crystals of chrysene (m. p. 245°) separated out. From these experiments, the authors conclude that chrysene has the following constitution:

$$\begin{matrix} C_{10}H_6—CH \\ | \quad\quad \| \\ C_6H_4—CH \end{matrix}$$

W. C. W.

Active Principle of Insect Powder. By G. Dal Sie (*Bull. Soc. Chim.* [2], **31**, 542—543).—From the ethereal extract of flowers

of pyrethrum the author has extracted two acids, one crystalline, the other an oily liquid of aromatic odour.

The acoholic extract yields a resinous body, resembling a glucoside, which is decomposed by sulphuric acid into a sugar and another product.

The author believes the active principle of the flowers of pyrethrum to be a volatile acid, existing in the powder in the free state.

L. T. O'S.

Nicotine and Nicotinic Acid. By R. Laiblin (*Liebig's Annalen*, 129—182).—The following modification of Schloesing's process for preparing nicotine is recommended:—Coarsely-cut tobacco is digested for a day with cold water, and the mixture subsequently boiled by injection of superheated steam, filtered, and the residue pressed. The same series of operations is repeated, and the mixed filtrates are evaporated to one-third of their volume. A quantity of lime, one-tenth of the weight of the tobacco used, is now added, and the mixture distilled by a current of steam as long as nicotine (recognised by its odour) comes over. The distillate is exactly neutralised by oxalic acid, the amount used being noted and evaporated to a thin syrup. The exact amount of potash necessary to neutralise the oxalic acid is now added, and the crude nicotine which separates is collected. The remaining liquid is exhausted with ether, and the nicotine thus extracted added to that first obtained. That portion of the crude base which distils over below 250° is converted into oxalate by adding powdered oxalic acid to its ethereal solution; and the purified oxalate, which separates as a syrup, after being washed with ether, is dissolved in water and again decomposed with potash as above. The product is finally heated to 110° for six hours by a paraffin-bath, and a slow stream of dry hydrogen passed through it to remove ammonia, ether, and water. The temperature is then gradually raised to 210° to complete the removal of the water, and on fractionally distilling the residue, pure nicotine comes over between 240—242°. It must be preserved in sealed tubes. One centner of tobacco thus treated yielded 600 grams of pure nicotine (=$1\frac{1}{2}$ per cent.), besides impure base.

Nicotine is not decomposed into well-defined simpler bodies by heating with hydrochloric acid at 280—300°. No addition-product is formed by the action of nascent hydrogen on the brominated hydrobromide, $C_{10}H_{13}N_2Br_5$.

Nicotine is readily oxidised by potassium permanganate in the cold, but only when the salt is added to its solution, as long as it is decolorised, is it possible to obtain crystalline oxidation-products. By employing a suitable process, which is fully described, potassium carbonate and nicotinate are the sole products found. The nicotinate is dissolved out by absolute alcohol, and converted into silver salt by precipitation. Nicotinic acid may be obtained from this by decomposing it with hydrogen sulphide.

Nicotinic acid was first obtained by Huber, by oxidising nicotine with chromic mixture, and was subsequently recognised by him as *carbopyridenic acid*, $C_5H_4N.COOH$ (*Ber.*, **3**, 849). Weidel also (*Annalen*, **165**, 328), by acting on nicotine with nitric acid, obtained an acid which he identified with Huber's, and which the author, by a

crystallographic comparison of salts, proves to be identical with his own; he, however, assigned to it the formula $C_{10}H_8N_2O_3$. By analyses of the acid and a variety of its salts (silver, calcium, potassium) and other compounds with hydrochloric acid and auric and platinic chlorides, the author decides in favour of Huber's formula. He also shows that when nicotinic acid is distilled with soda-lime, it yields a quantity of pyridene nearly equal to that which might be expected from a carbopyridenic acid. Moreover, nicotine yields carbopyridenic acid in almost molecular proportion.

Nicotinic acid forms crystalline compounds with hydrochloric and hydrobromine acids, of the formula $C_6H_5NO_2.HCl$ and $C_6H_5NO_2HBr$.

Ethyl chlorocarbonate acts violently on pyridene, but does not form ethyl nicotinate; the only products are ethyl chloride, ethyl carbonate, and pyridene hydrochloride. Neither is ethyl nicotinate formed by acting with ethyl iodide on silver nicotinate. When the compound of nicotinic chloride with hydrochloric acid (see below) is treated with absolute alcohol, a violent action occurs, and the product evaporated in a desiccator deposits crystals of nicotinic acid hydrochloride. The mother-liquor from these crystals gives with caustic soda an oily liquid, probably containing the ether, which no doubt existed in combination with hydrochloric acid.

If nicotinic acid, or, better, potassium nicotinate, is treated with phosphorus pentachloride, energetic action ensues, and a volatile crystalline compound sublimes, the analysis of which corresponds approximately with the formula $C_5H_4N.COCl.HCl$. This chloride is insoluble in ether, chloroform, benzene, and petroleum-ether. When heated with water it is reconverted into nicotinic acid; but no amide could be formed from it by the action of ammonia.

When the double chloride of zinc and nicotine, $C_{10}H_{14}N_2.2HCl + ZnCl_2 + 4H_2O$, is distilled with soda-lime, a large quantity of gas is given off, containing ammonia, methylamine, free hydrogen, and traces of hydrocarbons. The liquid distillate consists principally of nicotine, but contains also a considerable quantity of pyrrol, which was separated by fractional distillation, and analysed as the cadmium double salt. By carefully adding water to the fraction 245—270°, containing much nicotine, an oily liquid was separated, which, when dissolved in hydrochloric acid and fractionally precipitated by platinic chloride, gave a carmine-red easily-decomposable double salt, $(C_{10}H_{11}N.HCl)_2.PtCl_4$. The free base is a yellowish liquid of extremely penetrating and repulsive odour, boiling between 250—270°. The smallest quantity of it, dissolved in hydrochloric acid, gives an intensely red solution when boiled with platinic chloride. It is probably formed from nicotine by the direct separation of ammonia, $C_{10}H_{14}N_2 - NH_3 = C_{10}H_{11}N$.

Ch. B.

Oxidation-products of Quinine. By Z. H. Skraup (*Deut. Chem. Ges. Ber.*, **12**, 1104—1107).—When a solution of quinine sulphate, which has been acidified with sulphuric acid, is oxidised in the cold by potassium permanganate, it splits up into formic acid and *chitenine*, $C_{19}H_{22}N_2O_4 + 4H_2O$, according to the equation, $C_{20}H_{24}N_2O_2 + 2O_2 = C_{19}H_{22}N_2O_4 + CH_2O_2$. — Chitenine, which is identical with Kerner's *α-dihydroxyl-quinine* (*Zeits. f. Chem.*, 1869, 593), is separated from

the precipitated manganese dioxide by repeated lixiviation with boiling alcohol. It crystallises in colourless prisms, which are insoluble in ether and in absolute alcohol, but dissolve freely in acids and in water, to which a few drops of ammonia or potash have been added. Chitenine is a weak base; it forms the following compounds—

$$(C_{19}H_{22}N_2O_4)_2(H_2SO_4)_3 + 15H_2O,\ C_{19}H_{21}N_2O_4Ag,\ \text{and}$$
$$C_{19}H_{22}N_2.O_4H_2Cl_6Pt + 3H_2O.$$

Quininic acid, $C_{11}H_9NO_3$, is obtained by oxidising quinine with chromic acid, neutralising the product with baryta-water, and decomposing the barium salt with hydrochloric acid. On evaporating the solution, quininic acid separates out in prisms. The mother-liquor is treated with lead carbonate, and the lead salt decomposed by sulphuretted hydrogen. A non-crystalline syrupy liquid is thus obtained, which resembles the crystalline acid in its chemical properties.

W. C. W.

Constitution of Cinchonine Bases. By Z. H. Skraup (*Deut. Chem. Ges. Ber.*, **12**, 1107—1111).—The presence of a methoxyl group in cinchonine, cinchonidine, and quinine is indicated by the fact that when these bodies are oxidised, formic acid is produced, together with a substance possessing the properties of an alcohol or phenol, *e.g.*—

$$\underset{\text{Cinchonine and cinchonidine.}}{C_{18}H_{19}N_2.OCH_3} + O_4 = H.COOH + \underset{\text{Cinchotenine and cinchotenidine.}}{C_{18}H_{20}N_2O_2.OH}.$$

$$\underset{\text{Quinine.}}{C_{19}H_{21}N_2O.OCH_3} + O_4 = H.COOH + \underset{\text{Chitenine.}}{C_{19}H_{21}N_2O_3.OH}.$$

The author proposes $C_9H_6N.C_9H_{13}N.OMe$ as the formula for cinchonine and cinchonidine, and one of the three following formulæ for quinine:—

$$C_9H_4N(OH)Me.C_9H_{13}N.OMe,$$
$$C_9H_5NOMe.C_{10}H_{15}N.OH,\ \text{or}\ C_9H_5NMe.C_9H_{13}N(OH)OMe.$$

W. C. W.

Oxidation of Cholic Acid. By P. Latschinoff (*Deut. Chem. Ges. Ber.*, **12**, 852).—A notice pointing out the author's priority in this investigation. Though he has not yet obtained any definite results from the oxidation of cholic acid by potassium permanganate, he is of opinion that the production of the acid $C_{24}H_{35}O_{15}$, stated to have been obtained in this way by Dextrein, is very doubtful. The chief products of the reaction consist of acetic, carbonic, and oxalic acids, together with other acids richer in carbon.

T. C.

Bilic Acid, a New Oxidation-product of Cholic Acid. By E. Egger (*Deut. Chem. Ges. Ber.*, **12**, 1068—1070).—Tappenheimer (*Annalen*, **194**, 211 and 242) has shown that when cholic acid is treated with potassium dichromate and sulphuric acid, a mixture of cholesteric, cholanic, and fatty acids is formed. The author finds that by using a dilute oxidising mixture, viz., 60 grams of

potassium dichromate and 32·5 c.c. sulphuric acid diluted with eight times its volume of water, to 30 grams of cholic acid, a new acid (which he proposes to call *bilic acid*) is produced. The reaction is stopped when the product changes from a syrupy to a granular condition, and the hot solution filtered. Bilic acid, $C_{16}H_{22}O_6$, is deposited from the filtrate on cooling in white needle-shaped crystals, which dissolve freely in alcohol and in hot water. The acid melts when it is suddenly exposed to a temperature of 190°, but when gradually heated it is decomposed without melting. It is a bibasic acid, forming non-crystalline salts. On oxidation it yields a mixture of cholesteric and pyrocholesteric acids. W. C. W.

Chemical Composition of Peptones. By A. Kossel (*Deut. Chem. Ges. Ber.*, **12**, 703).—The author finds that fibrin-peptone contains less carbon (48·9 per cent.) than stated by Maly and Henninger (51·4 per cent.), and supposes that pepsin has a further action on the first-formed products, and that the composition of the products of digestion depends on the energy of the action of the pepsin. The objections of Herth (*Zeits. Phys. Chem.*, **1**, 277) to the author's earlier investigations are refuted. G. T. A.

Lecithin and Nuclein in Beer-yeast. By F. Hoppe-Seyler (*Deut. Chem. Ges. Ber.*, **12**, 702).—The author contradicts the statement of O. Löw (*Annalen*, **193**, 322), that nuclein and lecithin are not found in beer-yeast, and asserts that lecithin exists in all organisms hitherto investigated. About 81 grams of air-dried yeast gave 1·819 gram of bodies soluble in ether; among these were 0·2545 gram of lecithin in addition to 0·439 gram of cholesterin. G. T. A.

Physiological Chemistry.

Tension of Oxygen in Arterial Blood. By E. Herter (*Deut. Chem. Ges. Ber.*, **12**, 704).—The tension of the oxygen of arterial blood corresponds with an oxygen-pressure of 78·7 mm. of mercury, that is with half the partial pressure of atmospheric oxygen. As this tension is higher than that required at the temperature of the blood for the formation of oxyhæmoglobin, the author concludes that arterial blood contains only oxyhæmoglobin, and no hæmoglobin.

G. T. A.

Fattening of Sheep. By W. Henneberg, E. Kern, and H. Wattenberg (*Bied. Centr.*, 1879, 262—270).—The authors wished to ascertain the progressive increase in weight in full-grown sheep during fattening, the weights of the different parts of the slaughtered animals when cut up in the ordinary way, and the amounts of flesh, fat, sinew, and bone in these, in the case of sheep in the normal, moderately, and highly fattened conditions; and, lastly, the influence of a change of

diet on the fattened animals, when on the one hand a fodder relatively richer in nitrogen, on the other one relatively poorer, is given. The method of procedure was as follows:—Ten full-grown sheep were shorn on the 21st November, 1876, and set apart in five lots of two. Eight days later the weighings began and two animals were slaughtered. The other four lots received a full diet for some time until in good condition, when, after 70 days of fattening, lot 3 was slaughtered. Of the remaining three lots, lot 4 was treated with the same food as before, while lot 1 received a food poorer, and lot 2 a food richer in protein. The second period was extended until the last three or four weighings of the sheep became nearly constant. This point was attained after 77 days in the case of lot 1, but not until 56 days later in the cases of lots 2 and 4. The results obtained are given in the annexed table:—

First Period.—*From 28th Nov.*, 1876, *to 5th Feb.*, 1877, *ten weeks.*

	Lot 1.	Lot 2.	Lot 3.	Lot 4.
Weight of sheep at beginning ..	36·9	36·6	39·4	39·3
Ditto at end	48·6	47·5	49·5	49·5
Gain in weight	11·7	10·9	0·1	10·2
Ditto per week	1·17	1·09	1·01	1·02
Raw wool produced	0·8	0·9	0·9	0·9

Second Period.—*First Half: from 6th February, to 23rd April*, 1877, *eleven weeks. Second Half: from 24th April, to 18th June, eight weeks.*

	Lot 1.	Lot 2.		Lot 4.	
	1st half.	1st half.	2nd half.	1st half.	2nd half.
Weight of sheep at beginning	48·6	47·5	53·7	49·5	55·8
Ditto at end	48·7	53·7	56·5	55·8	57·8
Gain in weight	0·1	6·2	2·8	6·3	2·0
Ditto per week	0·01	0·56	0·35	0·57	0·25
Raw wool produced	0·8	0·8	0·4	1·0	0·6

The above table shows that the gain in weight in the case of lot 4 was in the first ten weeks 1·02 per kilo, in the following eleven weeks only 0·57, and in the last eight weeks not more than 0·25. The amount of food consumed also decreases, but not nearly in the same ratio. The lessening of the quantity of protein in the food seems to have been disadvantageous in the case of lot 1, whereas an increase of the amount had very little effect. It is also evident that the second fattening period would not be advantageous from a practical point of view.

The amount of flesh, fat, sinew, and bone was determined in the slaughtered animals. The results given below are the totals.

	Not fattened.	Moderately fattened.	Highly fattened.
Flesh	11·891	11·740	12·123
Fat	3·939	11·296	13·373
Bone	2·530	2·566	2·902
Sinew	2·488	1·818	1·992

This table shows that there is very little gain in flesh when full grown animals are fattened, the gain chiefly consisting of fat, the proportionate amounts of fat at the end of the three stages being 100 : 287 : 339. The composition of the flesh was the following: insoluble albumin, 15·85; soluble ditto, 1·29; extractive matter not albumin, 2·18; ash, 1·27; water, 79·41 per cent. J. K. C.

Beet-leaves as Fodder for Cows. By W. J. Kirchner and Du Roi (*Bied. Centr.*, **8**, 176—180).—Cows which were fed on beet-leaves yielded more milk per day than when the same cows were pasture-fed. The milk in the former case, however, contained a lower percentage of total solids and fat.

The cows, four in number, were first pasture-fed for four days, and the milk obtained from the two daily milkings was examined. The same cows were afterwards stall-fed, giving to each cow daily 25 kilos. of beet-leaves, together with other fodder. The average daily results obtained were as follows :—

	Average quantity of Milk per day from 4 Cows.	Specific Gravity.	Cream.	Total Solids.	Fat.	The daily yield of Milk contained.	
						Total solids.	Fat.
			p. c.	p. c.	p. c.	kilos.	kilos.
Pasture-feeding.		min. 1·0306 max. 1·0328	min. 8·5 max. 12·0				
Average	15·86	—	10·6	13·12	4·24	2·13	0·67
Stall-feeding on beet leaves.		min. 1·0312 max. 1·0338					
Average	21·05	—	10	12·98	3·84	2·73	0·807

Beet-leaves not only increase the yield of milk, but serve as a good nourishing fodder, as is shown by the increase in the weight of the cow :—

	No. 1. kilos.	No. 2. kilos.	No. 3. kilos.	No. 4. kilos.
After feeding on beet leaves..	485	513	420	380
Before „ „ ..	450	503	388	360
Increase	35	10	32	20

It is still an unascertained point to what extent stall-feeding without beet-leaves would affect these results. A. J. C.

Pancreatic Digestion. By E. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 701).—When human urine is distilled, a volatile substance passes over, the solution of which is coloured red to purple by nitric acid (*Pflüger's Arch.*, **2**, 364, and **16**, 309). A compound yielding the same reaction is produced by digesting albumin with pancreatic juice for 14 hours. It is also found in the small intestine and in the fæces. The author obtained during putrefaction of dried muscle and horn a crystalline acid, soluble with difficulty in water, but easily in alcohol and ether, and with a melting point of 76°, possibly α-paratoluic acid. During putrefaction of horny matter the formation of large quantities of phenol was also observed. G. T. A.

Digestibility of Nucleïn and Lecithin. By A. Bokay (*Bied. Centr.*, 1879, 112—114).—By the artificial digestion of nucleïn and lecithin, and by experimenting on dogs with substances containing them, the author has ascertained that nucleïn appears to be unacted on by the albumin-dissolving ferment of the pancreas, and that at least the greater part of the nucleïn introduced into the intestines is not absorbed in the organism. Lecithin, on the other hand, as was to be expected from its chemical constitution (on the supposition that it is composed of neurine, phosphoglyceric acid, and a fatty acid), is decomposed by the fat-decomposing ferment of the pancreas, and one product of its decomposition, phosphoglyceric acid, is reabsorbed.

A. J. C.

Oxidation in the Organism. By A. Takácz (*Deut. Chem. Ges. Ber.*, **12**, 699—700).—The author's object was to decide whether metamorphosis takes place in tissues when all the oxygen is withdrawn from the blood. Oxidation has been shown to continue in the animal organism for some time after death. This was proved by an experiment in which one of the hind legs of a rabbit was amputated immediately after tying the crural artery, the other 15 minutes after death. The first leg showed a larger amount of glycogen, sugar, milk-sugar, and fatty acids in its muscles than the second. In a second experiment, after amputation of a leg, the animal was poisoned by sulphuretted hydrogen in order to remove oxygen from the blood as quickly as possible. The second leg was removed ten minutes after death (which took place in 25—30 seconds). The two legs contained nearly the same amount of glycogen, &c. Hence the removal of oxygen from the blood seems to arrest chemical changes in the muscles. Glycogen disappears so rapidly from the muscles after death that it is all gone in 30 minutes, whilst after poisoning by sulphuretted hydrogen it is not lessened in that time. G. T. A.

Oxidations and Syntheses in the Animal Organism. By E. Baumann and C. Preusse (*Deut. Chem. Ges. Ber.*, **12**, 706—707).—Earlier investigations showed that phenol is partly converted in the body into phenylsulphonic acid; a peculiar chromogen was also observed in the urine, and after large doses of phenol a body was obtained which split up on warming with hydrochloric acid into phenol and an unknown substance (Baumann, *Pflüger's Arch.*, **13**, 291). A considerable quantity of phenol is converted in the body

into quinole, which is excreted in the form of sulphonic acid. More than a gram of pure quinol was obtained in six days from the urine of a dog to which phenol had been administered by painting it on the skin. Pyrocatechol seems also to be formed to a slight extent. Quinol is always found in the body after administration of potassium phenolsulphonate. After poisoning with stronger doses of phenol, a body is found in the urine which turns the plane of polarised light to the left. A similar substance is formed synthetically in the body, and appears in the urine after administration of nitrobenzene and other aromatic bodies (*Centr. Med. Wissench.*, 1875, 55), also after adding benzene and bromobenzene to the food. After administration of ortho-nitrotoluene, Jaffé obtained from the urine a lævogyrate body, *uronitrotoluic acid*, which reduced an alkaline copper solution.

G. T. A.

Composition of the Colostrum of the Cow. By W. Engling (*Bied. Centr.*, 1879, 214—217).—The first milkings, 3—4 litres, consist of a yellowish-white or reddish-brown (due to blood) viscous mass, which has a peculiar smell and sp. gr. 1·06—1·08. When freshly drawn the colostrum has an acid reaction, and on standing a layer of albumin forms on the surface, whilst the liquid underneath frequently keeps unchanged for 14 days. It coagulates to a cake when heated. The serum has a reddish opalescence, and is much similar in appearance to blood-serum. Cream is obtained from it with difficulty, only about 50—75 per cent. of it separating after long standing. The above properties are peculiar to the first milkings, as every subsequent milking produces milk which gradually approaches to the normal character, until after four days it has become quite normal.

Previous statements as to the character of the colostrum have been probably founded on milk which had been drawn from the cow at different periods of the milk's change in character. The sugar in colostrum crystallises with difficulty, and from its reactions appears to be grape-sugar, which the author has found always to be present to some extent in normal milk.

The fat is distinguished from ordinary milk fat by its peculiar smell, taste, consistency, and melting point (40—44°). It cannot be churned. From young cows the colostrum fat is of a more oily consistency.

Lecithin is present in large quantity, and can be so readily obtained in a crystalline form that it is suggested to employ colostrum milk as a source of this substance.

It contains 20 per cent. of albumin, which appears to be serum-albumin, containing less sulphur than egg albumin. Cholesterin, globulin, and about 2 per cent. of nuclein have also been obtained, and those substances which compose the nuclei of pus and blood corpuscles appear to form the nucleus of colostrum bodies.

Besides the above-mentioned substances, other proteïd bodies, resembling lacto-proteïn and peptone, are present. They are not coagulable, and are precipitated by tannic acid or alcohol, but do not appear to be peptones. Urea has been also obtained.

To detect urea in milk products, it is necessary that the evapo-

ration be made in a vacuum, to prevent the evaporation which easily occurs at ordinary temperature.

Analysis of colostrum from a cow eight years old gave the following results:—

Time after calving	Sp. gr.	Fat p. c.	Albumin p. c.	Caseïn p. c.	Sugar p. c.	Ash p. c.
Immediately after	1·068	3·54	16·56	2·65	3·00	1·18
After 10 hours	1·046	4·66	9·32	4·28	1·42	1·55
„ 24 „	1·043	4·75	6·25	4·50	2·85	1·02
„ 48 „	1·042	4·21	2·31	3·25	3·46	0·96
„ 3 days.....	1·035	4·08	1·03	3·33	4·10	0·82

The ash contained in 100 parts—

CaO.	MgO.	Fe_2O_3.	Potash.	Soda.	Cl.	Phosphoric acid.	Sulphuric acid.
34·85	2·06	0·52	7·23	5·72	11·25	41·43	0·16

At the end of three days albumin was no longer to be obtained from the milk by boiling. The transition from colostrum to normal milk takes place more slowly in the case of young cows, extending for 6—7 days after calving. A. J. C.

Behaviour of Potassium Salts in the Blood. By G. Bunge (*Deut. Chem. Ges. Ber.*, **12**, 703).—The author had supposed that a part of the potassium salt was first united with the blood corpuscles and was afterwards gradually given up to the ambient fluid and excreted. In order to determine whether potassium salts added to blood outside the body were entirely or partially taken up by the corpuscles or remained in the ambient fluid, fresh defribinated blood was mixed with potassium phosphates; after standing for 23 hours it was found that none of the salt had been taken up by the corpuscles, and that the latter retained their original composition unalterd. G. T. A.

Behaviour of Phenol in the Animal Organism. By E. Baumann (*Deut. Chem. Ger. Ber.*, **12**, 699).—The author determined the quantity of phenol contained in the urine of dogs to which it had been administered; this was effected by distilling the urine with hydrochloric acid. After daily doses of 0·24 gram of phenol, 53·8 per cent. of the whole could not be found in the urine; with doses of 0·12 gram 68·7 per cent.; and with doses of 0·48 gram 45·1 per cent. had disappeared. With doses of 0·06 gram only traces could be detected. The phenol did not seem to have been converted into oxalic acid, but probably was oxidised into carbonic anhydride and water. G. T. A.

Action of Amyl Nitrite on Blood. By P. Giacosa (*Deut. Chem. Ges. Ber.*, **12**, 703).—Jolyet and Regnard observed (*Gaz. Med.*, Paris, 1876, 340) that the blood became dark-coloured after inhalation of amyl nitrite, at the same time the spectroscope showed that the two

oxyhæmoglobin streaks became much fainter, while a distinctly dark streak appeared in the red. The author shows that the change depends on formation of metahæmoglobin, which, by treatment with ammonium sulphide and agitation with air, is reconverted into oxyhæmoglobin. When sodium nitrite is injected into the blood, the same phenomena are produced as on treating with amyl nitrite; nitric oxide acts in a similar but more energetic manner when inhaled.

see errata, p. 1168 G. T. A.

Chemistry of Vegetable Physiology and Agriculture.

A New Organised Ferment. By P. Miquel (*Bull. Soc. Chim.*, [2], **31**, 391—393).—In urine, besides the organised ferment discovered by Pasteur, and classified by Cohen as *Micrococcus ureæ*, the author has found another possessing the same property, namely, that converting urea into ammonium carbonate, and belonging to the class *Bacillus*. It consists of indentated filaments from 5 to 6 thousandths of a millimeter long and 7 to 8 ten-thousandths of a millimeter broad, which are sometimes isolated and sometimes connected, two, three, and four together. It resists a temperature of 65°, whilst *Micrococcus urea* dies when heated to 54—55°. Whether the *Bacillus* is the active principle of the *Micrococcus* or not requires further investigation.

L. T. O'S.

Action of the Ferment of Sour Wine on Good Wine. By J. Macagno (*Bied. Cent.*, 1879, 310).—The following are the main results of the investigation: The quantity of alcohol lessens as the fermentation goes on and the cream of tartar gradually disappears; the tannin is left unchanged; the principal volatile acids are acetic, metacetonic, butyric, and lactic acids. J. K. C.

Action of Alcohol on Bacteria. By Gunning (*Bied. Centr.*, 1879, 311).—The author finds that alcohol has not so deadly an influence on lower organisms as is generally supposed. J. K. C.

Occurrence and Vitality of Bacteria. Preservation of Yeast. (*Bied. Cent.*, 1879, 224—226).—Schaetzler has found two species of bacteria, *Micrococcus* and *Bacterium*, in a potable water at Lausanne and in cow's milk (both of which are said to have caused typhoid fever), as well as in the secretion of the mucous membrane in catarrh, and in urine.

Bretefeld states that amongst the lower organisms the spores of *Bacillus* are the least affected by heat. They are not destroyed by heating to a boiling temperature, and if after 15 minutes' boiling the liquid be cooled, the germination of the spores seems to be unaffected; after 30 minutes' boiling only a part germinates, but they are for the most part destroyed after the lapse of an hour. Above 100° they are

more readily destroyed; in 15 minutes when heated in a sealed tube at 105°; in 10 minutes at 107°, and in 5 minutes at 110°.

Solutions of carbolic acid, copper sulphate, &c., have no destructive action on *Bacillus*, but the germination of the latter is quickly arrested by mineral acids, tartaric and citric acids, and in a much less degree by acetic, butyric, salicylic, and carbolic acids.

The amount of acid in yeast has an important influence on its stability. It decomposes less quickly when the amount of acid which is formed during the fermentation has been allowed to remain in a greater proportion, that is, when less acid has been washed out. This observation suggested the addition of an acid, and nitric acid or tartaric acid, which is generally employed, is kneaded up with the pressed yeast, the amount of acid added being sufficient to make the total acidity equal to 2—5 per cent. By this means the yeast is rendered whiter, and never putrefies like ordinary yeast. A. J. C.

Influence of Atmospheric Electricity on Plants. By L. Grandeau (*Bied. Cent.*, 1879, 273—274).—The author brings forward some new results in addition to those already published (*ibid.*, **7**, 903). Two tobacco plants, one of which was placed in the cage mentioned in his former paper, and the other in the open, were in full bloom at the end of August; the latter bore 89 blossoms, the former only 45; in height and weight also the plant in the open was much superior to the other. J. K. C.

Ratio of Sugar in the Beet to the Phosphoric Acid in the Root and Leaves. By H. Pellet (*Bied. Cent.*, 1879, 183).—The opinion previously expressed by the author and P. Champion that there is a certain constancy in the proportion existing between the amount of sugar in the beet and the amount of phosphoric acid in the root and leaves, and between the sugar and the ash, is confirmed by Pagnoul and Barbet. The proportion of sugar to the phosphoric acid was stated by the author and Champion to be as 100 : 1·18—1·20.

Pagnoul's experiments show the proportion to be as 100 : 0·97 and 100 : 1·15, and it has also been ascertained that the addition of an excess of phosphates to some soils is of no advantage to increase the value of the sugar beet.

Barbet's results give the proportion as 100 : 1·28 and 100 : 1·15, and the proportion between the sugar in the beet and the ash (in the root and leaves) as 100 : 18·3. A. J. C.

Absorption of Atmospheric Nitrogen by Plants. By E. Gatellier (*Bied. Centr.*, 1879, 305).—Lucerne and corn were sown on a plot of land which had been as fully deprived of nitrogen as possible. The corn yielded a very poor crop, whereas the lucerne produced as much as if it had been sown in good land. The author concludes that it must have obtained its nitrogen from the air, but it is pointed out that the lucerne with its long roots may have obtained its supply from a deeper layer of soil. J. K. C.

Absorption of Water by Leaves. By F. Tschaplowitz (*Bied. Centr.*, 1879, 305).—A plant, the leaves of which had become withered from want of moisture, was brought into a warm damp atmosphere, the roots being at the same time protected from the action of the water. In a few hours the plant revived and the leaves assumed their original condition. J. K. C.

A Simple Experiment to Show the Evolution of Oxygen by Plants in Sunlight. By F. Hoppe-Seyler (*Deut. Chem. Ges. Ber.*, **12**, 702).—A glass tube $1\frac{1}{2}$ to 2 cm. wide, in which has been placed a fragment of *Elodea Canadensis*, is filled with water containing a little putrid blood and sealed up. If the blood is properly diluted, the two absorption-bands of oxyhæmoglobin are seen with the spectroscope. If the tube is left at ordinary temperature, the whole of the oxygen is used up by the putrefying blood and the living plant, and the band of hæmoglobin appears instead of the two former ones. If the tube is now exposed to direct sunlight, the absorption-bands of the oxyhæmoglobin reappear. This change in the spectrum may be repeated at pleasure for eight days: the action of light then becomes slower. It may be shown by this method that the living plant evolves no trace of carbon monoxide. G. T. A.

Nitrogenous Constituents of Young Grass and Hay. By O. Kellner (*Bied. Centr.*, 1879, 270—273).—It is a well-known fact that asparagine is very widely distributed in young plants; the author has therefore been induced to determine the quantity of nitrogen present in the form of amido-acids and acid amides in grass, at various stages of its growth. A field of meadow land was divided into three parts, the first being cut on the 14th May, the second on the 9th of June, and the last, in which the grass was over-ripe, on the 29th of the same month. Analyses of samples of these were made with the following results:—

	1st crop. p. c.	2nd crop. p. c.	3rd crop. p. c.
Proteïn	17·65	11·16	8·46
Fibre	22·97	34·88	38·15
Fat	3·19	2·74	2·71
Non-nitrogenous extract	40·86	43·27	43·34
Ash and sand	15·33	7·95	7·34
Nitrogen	2·824	1·787	1·354

The percentage of nitrogen present in the form of acid amides and amido-acids was in the first crop 31·6, second crop 13·4, and in the third crop 2·5 per cent. Nearly the third part of the nitrogen is therefore present in the first crop, in the form of a substance which scarcely possesses the nutritive value of the carbohydrates.

J. K. C.

Mineral Constituents of Horseradish. By A. Hilger (*Bied. Centr.*, 1879, 307).—The amount of water in the fresh roots is 83·45 per cent.; the dry roots contain 11·15 per cent. of ash, of which 72·54 per cent. was soluble in carbonic acid water. The ash contained:—Lime,

10·57; magnesia, 3·91; soda, 0·21; potash, 41·67; chlorine, 1·58; sulphuric acid, 16·49; carbonic acid, 11·62; phosphoric acid, 11·52; silica, 1·48; oxide of iron, 0·95 per cent. J. K. C.

Composition of Grapes at Different Stages of Ripeness. By B. Porro (*Bied. Centr.*, 1879, 308).—Analyses of must obtained from grapes gathered at various times gave the following results:—

Date. 1876.	Sp. gr. of must.	Grams per litre. Sugar.	Acid.	Cream of tartar.	Free tartaric acid.	Extractive matter.	Ash.
7 Aug. . .	1·0172	16·13	28·5	9·41	9·87	39·02	3·62
14 „ . .	1·0253	47·17	30·75	9·41	10·57	58·00	4·10
21 „ . .	1·0254	38·62	16·27	8·18	—	51·30	4·50
28 „ . .	1·0432	100·00	19·50	6·21	6·91	105·80	3·60
4 Sept. . .	1·0516	104·17	17·25	5·83	7·47	127·85	3·10
11 „ . .	1·0521	110·50	15·75	4·70	6·06	135·35	2·75
18 „ . .	1·0536	111·11	14·25	6·01	6·34	138·40	2·85
25 „ . .	1·0448	100·00	14·25	6·58	6·90	115·85	3·00
1 Oct. . .	1·0380	77·00	14·25	7·14	7·47	88·40	3·90

see errata, p. 1168

J. K. C.

Diseases of Cultivated Plants. (*Bied. Centr.*, 1879, 190—196).—G. Gibella has found that wheat may be infected with the fungi *Tilletia caries* and *Tilletia* [illegible] by simply bringing the seed into contact with their spores. The spores of *Sclerotium clavus* and *Ustilago carbo* do not seem capable of being similarly transferred.

The spores of *Tilletia* are more or less destroyed by cream of lime or a solution of copper sulphate, *e.g.*, a plot of land (1) was sown with non-infected wheat; plot 2 with infected seed; plot 3 with infected seed, which was subsequently treated for five minutes with cream of lime; plot 4 with infected seed after it had been steeped for five minutes in a $3\frac{1}{3}$ per cent. of copper solution. The resulting wheat from each plot contained respectively—

see errata p. 1168

	1.	2.	3.	4.
Sound ears	300	243	217	321
Blighted ears	—	197	18	2
	—	45	7	1 per cent.

Experiments on the propagation of the *Sclerotium clavus* endorse the results obtained by V. J. Kühn that it is not essential for this fungus to be in internal contact with the plant, but that its spores at once begin to vegetate on being transferred to the developing seed.

The maize fungus, *Tilletia Maydis*, is not capable of further propagation either through the seed or by direct transference to the female blossom.

The cabbage disease, which is known in Germany as cabbage goître, is attributed by Woronin to a fungus named *Plasmodiophora Brassicæ*.

In the first stage of the disease, the parenchyma of the root becomes abnormally large, and is filled with an opaque colourless plastic substance, by which the starch-granules are absorbed, and which represents the plasmodium of the new parasite. Later on the character of the cells is quite changed, the vascular tissues lie irregularly, and a greater part of the plastic substance has become globular in form, and is now said to be the spores of the fungus. The root then rots and the disease extends throughout the crop. Except precautionary measures such as careful selection of the young plant, destroying those deseased, and strict attention to rotation of crops on the land, there seems to be no remedy against this disease.

E. Rathay describes the vine disease, which is carried by the fungus *Cladosporium Roessleri*. The fungus first attacks the leaves, and is carried by them as they fall to the berries, which are thus infected. As they ripen they become hard at the stalk and shrivelled up at the upper half of the grape, which is of a plum-blue colour. The Gutedel variety of grape seems to be the source of the infection, as the fungus is not found in those vineyards where the Gutedel is absent.

G. Briosi has not succeeded in stopping the gum exudation of lemon trees by Gregorio's method, which consists in cutting away the whole of the affected part of the tree, and covering the wound and the upper part of the root which is laid bare for that purpose with flowers of sulphur. Further investigation is, however, necessary, as the age of the tree which is so treated seems to be important.

The disease of the mulberry tree, "male di Falchetta," has been ascribed by Gibelli to a fungus, *Agaricus melleus*, whilst Cesati believes it to be caused by the parasite *Protomyces violaceus*.

Gibelli and Antonelli have investigated the disease of the chestnut tree, in which the root decays and blackens, whilst the bark is very readily peeled off, and protuberances of free tannic acid occur on its inner layer and on the surface of the wood. They attribute the disease to a deficiency of potash in the soil. A. J. C.

Analysis of Weeds used as Salad. By F. H. Storer and D. S. Lewis (*Bied. Centr.*, 1879, 308).—The following plants were analysed:—Dandelion, cut on the 18th May; nettle, cut on the 22nd May; plantain, gathered on May 25th; and portulaca on July 14th; and white goosefoot on the 1st of August.

The fresh leaves contained—

	Dandelion.	Nettle.	Plantain.	Portulaca.	Goosefoot.
Water	85·54	82·44	81·44	92·61	80·80
Ash.....	1·99	2·30	2·16	1·56	3·02
Proteïn	2·81	5·50	2·65	2·24	3·94
Nitrogen-free extract	7·45	7·13	11·19	2·16	8·93
Fat.....	0·69	0·67	0·47	0·40	0·76
Cellulose	1·52	1·96	2·09	1·03	3·82

In view of the richness of these plants in proteïn, the authors think it strange that they should be neglected. J. K. C.

Nutritive Value of Seed-bearing Beetroot. By A. Leclerc (*Bied. Centr.*, 1879, 309).—According to the author's analyses, the roots lose by seeding a larger proportion of non-nitrogenous than of nitrogenous matter. J. K. C.

Oiling of Corn. By J. Pierre (*Bied. Centr.*, 1879, 310).—Corn is sometime shaken up with a little oil, to give it a better appearance: the author could not discover that this made any difference in the germination of the grain. J. K. C.

Carrot Seed. By A. Petermann (*Bied. Centr.*, 1879, 309).—Two specimens of carrot seed were analysed, one contained 12 per cent. and the other 16 per cent. of impurities; of 100 seeds sown of the first, 37 were good, and 32 of the second. J. K. C.

Choice of Beetroot for Seed. By G. Vibrans (*Bied. Centr.*, 1879, 309).—The specific gravity of beetroot immediately after gathering is a direct measure of the amount of sugar present in the root. J. K. C.

Seeds of Lallemantia Iberica. By E. Wildt (*Bied. Centr.*, 1879, 292—294).—Eighteen specimens of this planted yielded 225 grams of seed and 600 grams of straw and chaff. On analysis they were found to contain:—

	Seeds.	Straw and chaff.
Nitrogenous bodies	26·87 p. c.	14·06 p. c.
Fibre	16·35 „	32·87 „
Fat	29·56 „	2·78 „
Nitrogen-free extract	21·92 „	35·80 „
Ash	5·30 „	14·49 „

J. K. C.

Ridge Cultivation. By E. Wollny (*Bied. Centr.*, 1879, 250—254).—The heaping up of a quantity of loose earth round plants may have a very favourable influence on their growth. Many plants are capable of throwing out adventitious roots from the stem when the latter is in contact with moist earth, and the growth of these is greatly facilitated by the permeability of the loose soil to the atmosphere, whereby decomposition of the inorganic and organic constituents is facilitated, and the quantity of readily absorbable nutritive matter is increased. The soil on level ground easily clogs with the wet and becomes comparatively impermeable to the atmosphere, while ridges allow the rain to run down the sides. The conditions of temperature are also different: during the day, in warm weather, the soil in ridges is warmer than in the flat, because the surface which is exposed to the sun's rays is greater and more nearly inclined at a right angle to them, and although at night the cooling of the ridges is relatively greater, on account of the larger surface exposed, yet on the whole the mean temperature is greater. These statements the author has confirmed by several observations. The greater warmth of the soil is of importance to plants during the time of growth, in furthering the development of the roots and quickening the flow of sap: in this respect then, ridges

present some advantages over flat land. The relative quantity of water present in the two conditions of soil is also of great importance; in the case of ridges part of the rain runs down the sides, whilst that absorbed by the soil is easily evaporated, on account of the looseness, warmth, and greater surface, so that the soil in ridges retains generally 3 to 4 per cent. less water than that on the level. In the case of heavy wet soils this would be a decided advantage; but ridge cultivation would obviously not lead to good results where the soil is light and the climate dry, in which case the supply of water necessary for plants would be best obtained on the level ground.

J. K. C.

Potato Cultivation. By G. Drechsler (*Bied. Centr.*, 1879, 285—290).—The author has performed a series of experiments with the view of ascertaining the relation between the large and small potatoes in the seed and the crop, and finds that generally speaking large seed produces more large potatoes than small seed. J. K. C.

Cultivation of Dhurra or Sorgho Grass (Sorghum Saccharatum and Sorghum Vulgare. By J. Moser (*Bied. Centr.*, 1879, 189—190).—Four different fields were sown in May and manured with dung, superphosphate, and fish manure. The first cutting of the crop took place after 60 days' vegetation, and when the plant was 80 cm. high. The second crop was cut in September after 62 days' growing. The third crop was quite unimportant:—

Kilos. per hectare.	Sorghum Saccharatum.					Sorghum Vulgare.	
	1st crop.	1st crop.	2nd crop.	1st crop.	2nd crop.	1st crop.	2nd crop.
Undried substance	—	23460	23460	26480	7846	22510	6471
Dried substance	—	2993·5	3542·4	3508·6	1465·6	3027·6	1268·3
p. c.		13.01	see errata p. 1168				
Protein	6·52	~~130·1~~	9·45	9·70	9·32	10·27	7·91
Fat	2·29	3·60	4·16	3·47	4·12	4·80	3·33
Non-nitrogenous extractive matter	52·65	46·50	43·84	41·06	48·44	40·27	49·06
Vegetable fibre	30·93	26·39	31·56	31·82	30·20	30·51	30·73
Ash	6·25	8·93	8·81	10·82	6·30	12·45	6·85
Sand	1·36	1·57	2·18	3·13	1·22	1·70	2·12

It is quite possible therefore to obtain two good crops from the same sowing, and under very favourable conditions four cuttings have been obtained. As a green fodder cattle do not readily eat it on account of its strong odour. A. J. C.

Action of Rain on Clover Hay. By C. Brimmer (*Bied. Centr.*, 1879, 188).—One portion of clover hay (*a*) was allowed to lie on the

field during rainy weather for 14 days, and another portion of the same (*b*) was harvested under exceptionally favourable circumstances.

	Air dried.		Freed from sand and dried.	
	a.	*b.*	*a.*	*b.*
Moisture	10·90	10·24	—	—
Ash	4·28	4·51	4·82	5·03
Proteïn	15·30	16·03	17·23	17·89
Woody fibre	31·40	24·16	35·37	26·96
Non-nitrogenous extractives	35·90	43·09	40·49	48·10
Fat	1·90	1·81	2·14	2·02
Sand	0·32	0·16	—	—
Soluble in water	—	—	42·33	49·04

A. J. C.

Cultivation of Grass Seeds. By Otto and O. Knoch (*Bied. Centr.*, 1879, 290—292). The authors have made an investigation of the quality of the seeds of common creeping grass, and hope to extend their researches. J. K. C.

The Greenstone Soil of Berneck. By W. Knop (*Bied. Centr.*, 1879, 247—249). — This is a very fertile soil, which owes its origin to the weathering of the neighbouring greenstone; in analysing it and the mother-rock, the authors sought to ascertain the changes which took place during the weathering process. The chief results of their work may be thus stated: the greenstone in question contains about 50 per cent. of basic silicate soluble in hydrochloric acid, which has been to a large extent removed from the resulting soil and carried away as dust, leaving the soil richer in silica than the original greenstone, whilst the whole of the carbonate and part of the silicate of lime has been dissolved out by aqueous carbonic acid. On the other hand, the quantity of alumina is greater in the soil than in the greenstone, the alkalis remaining about the same. The soil possesses all the qualities necessary for vegetable growth.

J. K. C.

Temperature of Soils. By E. Wollny (*Bied. Centr.*, 1879, 161—164).—The results obtained from a long series of observations show that the average temperature of close soils is higher during the summer and lower in the winter or on a sudden decrease of temperature, than loose or porous soils.

During the day the mean temperature of close soils is higher, and at night usually lower than loose soils.

The temperature varies more considerably in close soils, and is more concordant in the two kinds of soils at the daily minimum, and differs most at the daily maximum. These differences in temperature between the two kinds of soils are due to the better conductibility of a close soil. A. J. C.

Influence of Time of Manuring in Beet Cultivation. By A. Ladureau (*Bied. Centr.*, 1879, 258—261).—The land used for the experiments was divided into 22 lots, two of which were left without manure. Of the rest every two lots were treated with various kinds of manure, one out of each two in winter and the other in spring, in order to ascertain the influence of the time of manuring on the yield. At the end of autumn the beetroot was gathered, samples from the various lots being taken and analysed. The author's conclusions are that a mixture of animal substance and phosphate gives the best results as regards the richness of the root in sugar, whilst nitrogen in the form of nitric acid gives the largest amount by weight of the root. Organic manures, such as rags, waste wool, roasted animal substances, &c., have a far more favourable effect when introduced at the beginning of winter than in spring, on account of their slow decomposition into easily absorbable matter. On the other hand, it seems more advantageous to apply artificial manures which contain nitrogen, phosphorus, and potash in a soluble form, shortly before the seed is sown. The largest yield by weight of the root is generally accompanied with the smallest percentage of sugar, and *vice versâ*.

J. K. C.

Agricultural Experiments on Irrigated Land. By F. Ullik (*Bied. Centr.*, 1879, 241—246).—The author was led to make some observations on an irrigated plot of land in Bohemia, because it did not yield so much produce as other lands in the neighbourhood which were not irrigated. Analyses were made of the water used for the purpose at the inflow and outflow, which gave the following results. The inflowing water (A) was found to contain a larger proportion of organic matter than the effluent water (B), whilst on the other hand, more non-volatile constituents were present in B than in A. Phosphoric acid, present in considerable quantity in A, was almost entirely wanting in B. Ammonia and nitric acid existed in larger proportions in B than in A, which was perhaps due to the oxidation of nitrogenous matter during irrigation. B always contained less alkali than A, a great part being absorbed by the soil. These results, which were obtained from a series of analyses, carried over a long period, were very constant. Analyses were also made of the first and second hay crops obtained in the year 1874. One kilo. of dried hay gave the following quantities of ash constituents in grammes:—

	Potash.	Soda.	Lime.	Magnesia.	Chlorine.	Phosphoric acid.
1st crop	19·45	1·06	16·36	5·21	3·45	5·88
2nd „	15·08	1·00	13·37	4·55	4·20	3·61

It is evident from these numbers that the quantity of chlorine present is more than sufficient to combine with the sodium, and must exist as chloride of calcium or magnesium, the potash being generally in combination with organic acids, which is rather remarkable, as these salts are known to act unfavourably on the animal system. In reference to the question whether the soil receives most of its mineral nutritive constituents from the dissolved or from the suspended substances in the water, the following facts are adduced. The total quantity of

potash and phosphoric acid present per hectare in the hay crop of one year amounted to 52 kilos. of potash and 14 of phosphoric acid, whilst the amount of these constituents extracted by the soil from solution was according to his analyses 54 kilos. of potash and 12·8 kilos. of phosphoric acid, which is nearly the equivalent of the former; the amount separated from the suspended matter in the water was only 9 kilos. of potash and 7 kilos. of phosphoric acid, showing that the land owed its fertility chiefly to the soluble constituents of the water. A reference also to the nitrogen confirms this, the quantity of nitrogen in the hay crop for that year being 41 kilos., whereas the nitrogen obtained from the suspended matter amounted only to 6 kilos. The author is of opinion that these facts will be found to hold good in other cases of irrigation. J. K. C.

Potassium Salts as a Manure. By Moser (*Bied. Centr.*, 1879, 302).—Potassium salts have been used for some time in Austria as manure, and have yielded so far better results than any other artificial manures. J. K. C.

Nitrates in Sugar Beets. By M. A. Ladureau (*Bied. Centr.*, 1879, 167—169).—Fremy and Dehérain have shown (this Journal, 1876, 955) that excess of nitrogenous manure decreases the production of sugar in the beet, and in a previous paper (*Annales Agronomiques*, 1878, **2**, 261—265) the author's results point to the same conclusion. He has now ascertained the amount of nitrogen existing in the sugar beet as nitrate, and the influence of manures containing nitrogen in the form of organic nitrogen, ammonia, and as nitrate respectively, on the production of nitrates in the beet. The results which are given in a series of tables, show that the beets which contain the most sugar are poorest in nitrates, and that at the same time the juice contains the smallest amount of mineral salts.

The results obtained when an equal amount of nitrogen was added to each plot of land through different kinds of nitrogenous manure show their influence on the production of nitrates in the beet. The manure containing nitrogen as ammonia produced the smallest amount of nitrates; on the other hand, manure wherein the nitrogen existed as nitrates increased the nitrates in the beet, and decreased the amount of sugar.

It is necessary, however, to ascertain by direct experiment the effect of manuring the soil with a large excess of nitrates, as in some of the experiments the addition to the soil of a large quantity of nitrogenous manure free from nitrates, had produced, through nitrification in the soil, more nitrates in the sugar-beet than manuring the soil with nitrates themselves. A. J. C.

Effect of Manure on Crops. By W. Christiani (*Bied. Centr.*, 1879, 164—166).—These experiments show the quantity of produce which was obtained from manured and unmanured land during a period of five years, and the quality of the crops produced by the land in the last two years.

Experiments had been carried out on the same plots for 45 years

previously (*Bied. Centr.*, 1872, 207), Plot II*a* remaining unmanured during the entire period of 50 years.

The manure employed was ordinary farmyard manure, and was applied to the land at the turnip crop (1872 and 1875) in centners 1 = 110¼ lbs.) per morgen (3,054 sq. yds.) as given at the head of the table:—

		Plot I.		Plot II*a*.		Plot II*b*.		Plot III.	
		1350 centners manure.		900 centners manure.		Unmanured.		900 centners manure.	
		Produce per hectare.							
		Corn and turnips.	Chaff and straw.	Corn and turnips.	Chaff and straw.	Corn and turnips.	Chaff and straw.	Corn and turnips.	Chaff and straw.
		kilos.	kilos.	kilos.	kilos.	kilos.	kilos.	kilos.	kilos.
1872	Turnips (with manure).....	48906	—	43452	—	18468	—	44964	—
1873	Barley	3294	5742	3312	5256	2934	4662	3096	4878
1874	Spring wheat ...	1880	5696	2304	5850	2160	4788	2070	5094
1875	Turnips (with manure).....	54108	—	46008	—	15876	—	176376	—
1876	Barley.....	2682	4770	2556	4708	1764	3456	2412	4140

Quality of the Produce obtained during the last two years from manured and unmanured Land in Kilograms per Hectare.

	Turnip crop. 1875.		Barley crop, 1875.					
			Plot I.		Plot II*b*. Unmanured.		Plot III.	
	Plot I.	Plot II*b*. Unmanured.	Corn.	Straw and chaff.	Corn.	Straw and chaff.	Corn.	Straw and chaff.
Organic substances ...	9036	2444	2200	3712	1466	2686	2002	3238
Sugar.....	5736	1572	—	—	—	—	—	—
Starch.....	—	—	1598	—	1054	—	1430	—
Fibre.....	—	—	92	1416	82	998	94	1204
Albuminoïds.....	758	222	304	124	172	104	236	112
Mineral constituents..	324	96	78	376	46	276	66	310
Potash.	135·2	35·0	17·2	63·8	13	23·4	19·8	18·6
Phosphoric acid.....	37·8	11·2	25·4	9·0	9·8	15·8	21·0	9·2

Although Plot II*b* had been unmanured for 50 years, it will be seen that the land has produced crops of normal growth judging from the proportion of organic substance to the potash in the turnips (Plot I being 1 : 67, and Plot II*b* 1 : 70) and to the phosphoric acid in the case of the barley (Plot II*b* 1 : 87; Plot III 1 : 95). A. J. C.

Effect of Artificial Manures on the growth of Barley and Meadow Land. By Doring and Bochmann (*Bied. Centr.*, 1879, 171—172).—*On the growth of Barley.*—Each plot of land manured was ½ morgen (1,527 sq. yds.) in area, and the soil was a sandy loam with a slightly calcareous subsoil.

	Plot I. Unmanured.	Plot II. ½ Centner (55 lbs. avoir.) superphosphate.	Plot III. ½ Centner superphosphate with ¼ centner Chili saltpetre as top dressing.	Plot IV. ½ Centner Chili saltpetre.	Plot V. ¼ Centner Chili saltpetre as top dressing.
	lbs.	lbs.	lbs.	lbs.	lbs.
Corn	318	293	419	509	388 ~~308~~
Chaff	99	89	109	151	110
Straw.....	372	345	518	550	494

see errata p. 1168

Meadow Land manured with Kainite. Each Plot = ½ Morgen.

	No. 1. Without manure.	No. 2. ½ Centner of kainite.	No. 3. 1 Centner of kainite.
	lbs.	lbs.	lbs.
Hay (first cutting)....	220	152	163

The crop of hay from the second cutting again showed that no advantage was gained by the use of the kainite.

The weight of produce is expressed in German pounds. No analyses of the manures are given in the paper. A. J. C.

Analytical Chemistry.

Contributions to Quantitative Spectrum Analysis. By H. Settegast (*Ann. Phys. Chem.* [2], **7**, 243—271).—The author's results show that chromic acid is completely expelled from its salts by all the acids employed (sulphuric, formic, acetic, butyric, and tartaric), except carbonic acid. The degree of dilution of the solution, and the quantity of acid present, have no effect. These results agree completely with the heats of neutralisation of these acids as determined by Thomsen (*Pogg. Ann.*, **143**, 497).

For the purpose of determining small quantities of nitric acid spectroscopically, use is made of the reaction which occurs between the sulphuric acid solution of diphenylamine and nitric acid. Other circumstances being the same, the intensity of the blue colour thus produced depends on the amount of nitric acid present; the absorption spectrum is also constant for a given depth of colour. The "extinction coefficient" of such a solution having been found, the amount of nitric acid present may be calculated. This method serves for the estimation of nitric acid in waters.

An analogous method is also described for the estimation of phosphoric acid, which depends on the well-known reaction of phosphates with uranous salts. This method, although it gives good results, is not so simple as might be desired.

Ample details of the processes are given in the original paper.

T. C.

Volumetric Estimation of Fluorine. By S. L. Penfield (*Chem. News*, **39**, 179—180).—The method is based on the equation $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$. The hydrofluosilicic acid is precipitated by potassium chloride and the liberated hydrochloric acid titrated with standard alkali.

Process.—The fluoride is weighed out into a flask of 150 c.c. capacity and 10 grams of powdered and ignited quartz is added, together with two or three pieces of quartz about the size of kidney beans, and 30—40 c.c. of sulphuric acid, which has been previously heated and allowed to cool. The flask is closed by a cork carrying two tubes, one dipping beneath the liquid and communicating with a gasholder containing air, the other for the exit of the silicon fluoride. The contents of the flask are heated at 150—160° C. for two hours, during which time from 5 to 6 litres of dried air are bubbled through the liquid. The silicon fluoride mixed with air passes first through a small **U**-tube immersed in water in order to condense any sulphuric acid mechanically carried over, and next into a **U**-tube 18 cm. long, and 2·5 cm. diameter, connected with a smaller **U**-tube, both containing a solution of potassium chloride mixed with an equal volume of alcohol. When the decomposition and aspiration are completed, the contents of the two **U**-tubes are titrated with standard alkali, litmus or cochineal being used as an indicator. A few c.c. of alcohol should be added before titrating, or standard alkali may be used which contains half its volume of alcohol. Each equivalent of sodium carbonate used corresponds with six atoms of fluorine ($Na_2CO_3 = H_2SiF_6$).

When the mineral in which fluorine is to be determined contains chlorine (*e.g.*, apatite), a **U**-tube containing pumice saturated with anhydrous copper sulphate is substituted for the empty **U**-tube. The results obtained by the author with quantities of fluorspar varying from ·1804 gram to 1·013 gram are very satisfactory.

J. M. H. M.

Estimation of Nitrogen in Urine. By W. Schröder (*Deut. Chem. Ges. Ber.*, **12**, 704).—The amount of nitrogen in urine as estimated by addition of an acid and evaporation to dryness in a vacuum agrees with that obtained by adding an acid and evaporating on the water-bath at 100°. Seegen's method (impregnating soda-lime with

the urine, incinerating in a bulb of hard glass, and absorption of the ammonia by an acid) gives too small a value for the nitrogen.

G. T. A.

Behaviour of Ammonium Chloride in the Organism and Estimation of Chlorine in Urine. By E. Salkowski (*Deut. Chem. Ges. Ber.*, **12**, 700).—Feder (*Zeits. f. Biol.*, **13**, 256, and **14**, 161) concluded that the total amount of ammonium chloride administered to a dog was excreted unchanged in the urine. The author thinks that a part of the nitrogen is excreted in the form of urea. The estimation of chlorine in urine containing considerable amounts of ammonium salts by evaporation and incineration with saltpetre gives too low a value: the error is lessened by adding a gram of sodium carbonate for every 10 c.c. of urine before evaporation. G. T. A.

Determination of Lithium. By C. Rammelsberg (*Ann. Phys. Chem.* [2], **7**, 157—158).—The common method of determining lithium by precipitation with phosphoric acid and caustic soda is inexact, since the precipitated phosphate always contains sodium, even when a very slight excess of soda is employed.

The method proposed many years ago by the author (*Pogg. Ann.*, **66**, 85), gives much better results. This method consists in separating the chlorides of sodium and lithium with a mixture of equal volumes of ether and alcohol. T. C.

Law Peculiar to Metallic Ferrocyanides. By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 436—437).—Those metals whose hydrates are soluble in ammonia or ammoniacal salts, are for the most part completely precipitated by potassium ferrocyanide in presence of ammonium tartrate, whereas those metals which are precipitated by ammonia in presence of ammoniacal salts, but whose hydrates are soluble in ammonium tartrate, are not precipitated by potassium ferrocyanide in presence of ammonium tartrate, as the following table shows:—

Oxides soluble in Ammonia or Ammoniacal Salts, precipitated *by K_4FeCy_6 in presence of Ammonium Tartrate.*	*Oxides insoluble in Ammoniacal Salts but soluble in Ammonium Tartrate* not precipitated *by K_4FeCy in presence of Ammonium Tartrate.*
Barium (white)	Iron (ferric)
Calcium ,,	Manganese (Mn_2O_3)
Magnesium ,,	Lead
Zinc ,,	Tin (SnO and SnO_2)
Cadmium ,,	Bismuth
Nickel (pink)	Antimony ($SbCl_3$ and $SbCl_5$)
Cobalt (yellow)	Vanadium (V_2O_3 and V_2O_4)
Copper (red or ochre)	Titanium (TiO_2)
Iron (FeO), green, changes to white, rapidly oxidises, becoming pink, finally blue.	Uranium (U_2O_3)
Manganese (MnO), white	Aluminium
Mercury (HgO), ,,	
Silver ,,	

L. T. O'S.

Characteristic Colour Reactions produced by the Action of Antimony or Bismuth Trichloride on the Aromatic Hydrocarbons. By WATSON SMITH (*Deut. Chem. Ges. Ber.*, **12**, 1420).—The reactions are thus obtained with *antimony trichloride*:—

A small quantity of the crystallised salt is placed in a small porcelain crucible, and melted, and then further heated over a small flame. A small particle of the substance of which the reaction is required is then allowed to fall upon the inner side of the crucible, which is so inclined that the fused chloride comes into contact with it. Fusion follows, accompanied in certain cases by a coloration. On setting the crucible upright again, the coloured spot elongates, and becomes more evident as a coloured stripe.

Naphthalene.—Chemically pure (sublimed)—no coloration. On cooling, beautiful rhombic tables are formed and float in the fused menstruum. The formation of these is characteristic of naphthalene. If in the slightest degree impure, naphthalene produces a more or less beautiful carmine tint with the fused antimony trichloride.

Anthracene.—Traces give a yellowish-green tint. On cooling, colourless needles are formed of an addition-product of anthracene and antimony trichloride, and apparently characteristic for the former.

Phenanthrene does not dissolve in the chloride so easily as anthracene. A faint greenish coloration is produced.

Diphenyl and the *three dinaphthyls* give no coloration.

Stilbene.—The fusion is to be at little more than blood heat. The smallest trace of hydrocarbon then gives an orange coloration, easily disappearing on stronger heating, and even with a considerable proportion of stilbene.

Phenyl-naphthalene (the β-isomeride in all probability), gives no coloration.

Triphenylmethane.—No colour. If excess be employed a greenish tint.

Chrysene.—Traces only produce a golden-yellow tint.

Pyrene.—Not so easily dissolved, and gives a faint greenish coloration.

Bismuth trichloride.—Naphthalene.—According to its impurity, a more or less deep orange coloration. Quite pure, no coloration. On cooling, yellow transparent lanceolate needles separate out before solidification of the whole mass, most probably of an addition compound of the trichloride with naphthalene.

Anthracene.—Purple-black coloration. Very characteristic.

Phenanthrene.—Either brown or greenish-brown tint.

Diphenyl and Dinaphthyls.—No reaction.

Antimony trichloride and the Alkaloïds:—Conine and Nicotine.—No coloration.

Morphine and Codeine.—Traces give no tint, larger quantities a faint greenish colour.

[*Apomorphine.*—No reaction.]

Narcotine.—The trichloride is heated till it begins to fume. Traces of the alkaloïd then give a deep olive-green tint, almost black.

Thebaïne.—The fused chloride should be only so hot that the crucible can just be held in the hand. Traces give a blood-red coloration, disappearing at once on further heating, even when considerable quanti-

ties are added. If heated to incipient ebullition of the trichloride, the tint changes to greenish-brown.

Papaverine, *strychnine*, *quinine*, *cinchonine*, *atropine* give no colorations.

Narceine.—Small quantities give a sulphur-yellow coloured stripe, when the crucible in inclined.

Brucine.—With the smallest traces, a beautiful deep-red or purple-red colour, at first appearing nearly black. Easily produced even in the almost boiling trichloride.

Veratrine.—Brick-red tint, disappearing on further heating. On using more than very small quantities, the colour only partially disappears at a higher temperature.

Aconitine.—A bronze-brown coloration.

Santonine.—If even considerable quantities be added, no tint is produced till the trichloride is heated to incipient ebullition, when a very characteristic deep bluish olive-green tint appears.

Brucine can be easily detected in the presence of the other alkaloïds, producing a red tint, since a trace added at an incipient boiling temperature gives a stable red tint. The veratrine tint does not disappear (a tolerably large quantity being added) nearly so easily as the thebaïne tint. W. S.

Influence of Temperature on the Deviation of Polarised Light by Solutions of Inverted Sugar. By P. Casamajor (*Chem. News*, **39**, 212—214, 234—236).—The observation that the action of inverted sugar solutions on polarised light varies with the temperature is due to Mitscherlich. In 1849 Clerget proposed (*Ann. Phys. Chim.*, **26** [3], 175) when testing commercial sugars by Soleil's saccharimeter, to determine the rotatory power of the sugar solutions after inversion with hydrochloric acid, and thus eliminate the error in the direct test caused by the presence of optically active substances other than cane-sugar. The original deviation (D) of a solution of crude cane-sugar may be made up of four factors, viz.:—that due to the cane-sugar (+ C), to inverted sugar ($-i$), to dextrorotatory impurities ($+h$), and to lævorotatory impurities ($-g$). That is, $D = C - i + h - g$. Supposing the substances producing the deviations $-i$, $+h$, $-g$ to undergo no sensible change in their optical activities when the cane-sugar in the solution is inverted by heating with hydrochloric acid, if the deviation caused by the solution after inversion (d) be observed, we have $d = -I - i + h - g$, where $-I$ represents the deviation caused by the inverted sugar corresponding with the cane-sugar originally present. Subtracting the second equation from the first, we have $C + I = D - d$. By a series of experiments Clerget established the relation, which varies with the temperature, between C and I. For temperatures between 10° and 35° C., a range suited for all practical purposes, he constructed a table, from which we find that at 10° the quantity $D - d$ (*i.e.*, the *arithmetical* sum of the deviations before and after inversion) corresponding with 100 parts of pure cane-sugar is 139, and for any temperature $t°$ between 10° and 35°, $D - d = 139 - \frac{t - 10}{2}$.

Assuming this formula of Clerget's to hold for temperatures below 10°, the value of D − *d* at 0° would be 144. This means that a solution of cane-sugar which produces a positive deviation of 100 divisions on the saccharimeter scale, will, after inversion by being heated with 10 per cent. of hydrochloric acid and correction for the volume of acid added, produce a negative deviation of 44 divisions of the scale.

Again, supposing Clerget's law to hold good also for temperatures above 35°, the negative deviation of an inverted solution obtained from 100 cane-sugar would be expressed by the formula—

$$d = -\left(44 - \frac{t}{2}\right).$$

This relation between *d* and *t* is of the form $y = mx + b$, the equation of the straight line. If the law it expresses holds good to the end, the temperature at which the deviation caused by a solution of inverted sugar becomes 0 should be 88° C. This temperature as given by some authors is 90°, and recently Ricketts has stated it to be 91·7°.

In order to ascertain whether the temperature deduced from Clerget's table, or that given by Ricketts, is the correct one, the author has made a number of observations with inverted pure cane-sugar at various temperatures from 14° to 92°, with the result of completely confirming the truth of the formula deduced from Clerget's table, according to which the temperature of no deviation is 88°. He also quotes in a footnote the following formula :—

$$\mathrm{D} - d = 144{\cdot}16035 - 0{\cdot}50578\ t,$$

which results from the experiments of Tuchschmid (Scheiber's *Zeitschrift*, 1870, 649), and which is practically identical with the one given above.

The most convenient plan for correcting sugar-test by inversion is the following :—

The sugar solution is placed in the saccharimeter, and the saccharimetric test, D, noted down. To a portion of this solution, say 50 c.c., is added one-tenth of its volume of concentrated hydrochloric acid. The graduated flask containing the mixture is heated in a water-bath to 68° C., an operation which should take about 10 minutes. The solution is then immediately cooled to a temperature between 10° and 35°, and placed in a thick glass tube provided with a vertical tubulure for the insertion of a delicate thermometer. This tube is made 22 cm. long instead of 20 cm., so as to compensate for the volume of the hydrochloric acid. If now the negative deviation *d*, and the temperature *t* be observed, the correct quantity, C, of cane-sugar will be given by the formula—

$$\mathrm{C} = \frac{100\ (\mathrm{D} - d)}{144 - \frac{t}{2}}.$$

The author gives a series of 28 consecutive tests of raw and refined sugars, before and after inversion. In some cases the difference between the corrected quantity of cane-sugar and that given by the

direct test before inversion, amounts to 3 or 4 per cent. When the test before inversion is lower than the corrected test, the presence of an excess of lævorotatory impurity is indicated, and when higher, it is due to an excess of dextrorotatory impurity. J. M. H. M.

Examination of Pavy's Method of Determining Glucose. By O. Hehner (*Chem. News*, **39**, 197).—The ammoniacal Fehling solution recommended by Pavy (*ibid.*, **39**, 77) for estimating glucose, is made by mixing 120 c.c. ordinary Fehling solution with 300 c.c. ammonia (sp. gr. ·88) and diluting to 1000 c.c. 100 c.c. of this liquid, containing 12 c.c. Fehling solution are capable, according to Pavy, of oxidising 0·05 gram glucose.

The author describes experiments which show that the amount of glucose oxidised by the Pavy solution is influenced to a large extent by the amount of sodium hydrate present, and that the ratio given by Pavy holds good only when the ammoniacal copper solution contains from 80 to 150 grams sodium hydrate per litre. Pavy's solution made from the ordinary Fehling solution recommended by Fresenius will contain only 68 grams NaHO per litre, and will give higher results in determining glucose (using Pavy's numbers) than the ordinary Fehling solution. If, on the other hand, the Pavy solution contains much more than 150 grams soda per litre, the results will be too low. With ordinary Fehling solution 1 mol. of glucose requires 5 mols. of cupric oxide for oxidation; with the ammoniacal solution containing 120—150 grams NaHO per litre, 6 mols. of cupric oxide are required; and with ammoniacal copper solution containing no soda, the reaction proceeds very slowly and requires 8 mols. cupric oxide. If the Pavy solution contains the proper quantity of sodium hydrate the process is very satisfactory, and the termination of the reaction is exceedingly sharp.

The above remarks apply only to the determination of dextrose and lævulose. Milk-sugar appears to reduce less cupric oxide in Pavy's solution than in Fehling's solution, and its estimation with the former is even more unsatisfactory than with the latter.

J. M. H. M.

Reactions of Albumin, and Behaviour of the Albumin of the Refracting Media of the Eye. By J. Dogiel (*Pfluger's Arch. f. Phys.*, **79**, 335—342).—Adamkiewicz (*ibid.*, **9**, 156) has observed that sulphuric acid of 1·8095 sp. gr. produces various colours when mixed with albumin—green, yellow, orange, red, or violet, according to the amount added. The same colour-reactions are better produced by a mixture of acetic and sulphuric acids, which furnishes a sensitive test for albumin.

The lens of the eye gives a violet colour when treated first with acetic, and subsequently with sulphuric acid; and the same colour is produced by a mixture of hydrochloric and sulphuric acids, or, on warming, with fuming hydrochloric acid alone. A violet colour is also produced when hydrochloric acid is added to the lens soaked in acetic acid, and the mixture exposed for some days to the air.

These colours probably depend on oxidation, for they are produced, although not always in the same order, when ozone is passed

through a solution of the lens in hydrochloric and acetic acids, the final shade being yellow. When fuming hydrochloric acid is used, a violet colour is rapidly produced by oxygen. The whole series of colours from green to yellow may be obtained when the mechanically divided lens is suspended in acetic acid, treated with ozone until the mixture becomes yellow, and fuming hydrochloric acid then added. If, on the other hand, the lens is suspended in water and treated with ozone until the albumin separates as a tenacious mass, colours are not produced on adding the mixed acids. The coloration of albumin by nitric acid, too, is probably due to oxidation.

Albumin is contained in the cornea, aqueous and vitreous humours, and lens of the eye. The author concludes that the aqueous humour does not consist of lymph, since the amount of albumin contained in it is not altered by a change in the blood pressure, however produced. Ch. B.

Estimation of Hæmoglobin and Oxygen in Blood. By G. Hüfner (*Deut. Chem. Ges. Ber.*, **12**, 702).—The author obtains the "absorption ratios" of hæmo- and oxyhæmo-globin by means of his spectrophotometer (*J. pr. Chem.*, **16**, 290). These and the extinction-coefficients of this part of the spectrum being known, the amount of hæmoglobin, &c., may be estimated. G. T. A.

Determination of Fibrin. By W. Henneberg (*Bied. Centr.*, 1879, 303).—It appears that the more finely a substance under investigation is powdered, the less will the percentage of fibrin be found to be. It is therefore suggested that some degree of fineness be fixed upon as a common basis in all analyses of fodder. J. K. C.

Detection of Lecithine. By O. Loew (*Pflüger's Arch. f. Phys.*, **79**, 342—346).—In spite of the strictures of Hoppe-Seyler (*Zeits. f. Phys. Chem.*, 1878, 428), the author maintains his assertion (*Annalen*, **193**; *J. pr. Chem.*, 1878) that lecithine is not contained in yeast. Hoppe-Seyler appears to have proved its presence and calculated its amount by estimating the phosphoric acid contained in the ethereal extract of yeast.

The author, however, finds that monopotassic phosphate (which exists in yeast) is soluble in ether to the extent of 3 mgrms. in 100 c.c.; and this solution, when mixed with alcohol and evaporated, leaves potassium ethyl-phosphate, which does not respond to the ordinary tests for phosphoric acid until it has been ignited.

Neither lecithine nor glyceri-phosphoric acid can be detected in the fatty extract of yeast prepared by a mixture of absolute alcohol and ether. The small quantity of watery residue obtained contains a considerable quantity of monopotassic phosphate. After removal of this by baric chloride and ammonia, a mere trace of phosphoric acid is found on evaporation and ignition. Ch. B.

Technical Chemistry.

Photo-lithography. By A. Ott (*Dingl. polyt. J.*, **232**, 44—50).—Photo-lithography is a process by means of which a picture produced by exposure to the light may be transferred to and fixed on lithographic stones, or by which a layer made sensitive to the light is spread over the stone, exposed under a negative, and developed. Although its application is more limited than that of phototype, photo-lithography is nevertheless largely used for copying drawings, plans, engravings on steel and copper, wood-cuts, and maps. Coloured drawings, however, cannot be copied.

According to Husnik, gelatin-paper, as it is brought into commerce, may be used. He also gives directions for the preparation of a photo-lithographic paper which may be rendered sensitive when required for use. The following solution is employed. 1 part of ammonium dichromate, 15 parts of water, and 4 parts of alcohol are mixed together, and the mixture is treated with ammonia until it smells of it. This solution must be kept in the dark in a well stoppered bottle.

It is essential to use sharp negatives. With regard to the exposure of the sensitised paper, it is stated that, after the paper has been firmly fixed to the negative, sunlight gives sharper pictures than diffused light; in the former case one to three minutes' exposure suffices, in the latter case ten to thirty minutes are required. Before developing the picture, the paper is coated with the following solution. 8 parts white wax, 2·5 parts best neutral soap, 1 part ignited lampblack, and 2 parts light-coloured shellac are boiled with water to a stiff paste, which is thinned with turpentine, or a fat lithographic ink may be employed mixed with one-sixth of wax, and made of an oily consistence by addition of turpentine. This solution is carefully brushed over the paper by means of a sponge, and after drying it is allowed to soak in water for ten minutes, and the picture is then developed by brushing the paper with a soft sponge with a continuous circular motion. When the picture has been fully developed, the paper is washed with water and pressed between blotting-paper. The moist paper is then placed with its picture side on a clean cut lithographic stone, covered with several sheets of paper, and pressed slightly in the beginning, the pressure being increased gradually. The paper is then removed from the stone, when the picture will be found fixed on the latter. D. B.

Hectograph and Chromograph. By V. Wartha (*Dingl. polyt. J.*, **232**, 81—83).—These apparatus have been used in commerce for some time for the preparation of copies. The original is written on ordinary well glazed paper with a thick aniline ink. It is only necessary to place the written side of the paper on an elastic cake contained in a tin box, to rub the flat hand over it several times, and then to remove the paper. In this way the greater part of the ink is absorbed by the cake, from which 40 to 50 copies can be obtained. The composition for hectographs consists of a mixture of gelatin, syrup, glycerol,

and acetic acid. The latter renders the gelatin somewhat soluble, whilst the syrup and glycerol prevent the hardening of the gelatin. For chromographs the following mixture is used. 100 grams of the best gelatin are melted with 400 to 500 c.c. of a thick precipitate of barium sulphate in a basin on a water-bath, 100 grams dextrin are added with constant stirring, and finally 1,000 to 1,200 grams of glycerol. After cooling the mixture sufficiently, it is poured into a flat tin box, and allowed to solidify. In order to remove the ink from chromographs, cold water is used, whilst hectographs require warm water. Poirrier's "violet de Paris" forms the best ink. D. B.

Carbon Bisulphide Manufacture in Swoszowice, and its use for the Extraction of Sulphur. By S. Mrowec (*Dingl. polyt. J.*, 232, 86).—The author mentions that Winkler (*ibid.*, 228, 366) was the first who introduced the idea of the production of carbon bisulphide, and the extraction of the sulphur from the sulphur beds by means of carbon bisulphide, in the Swoszowice district. The practical details, however, were worked out by the author.

He rectifies Winkler's statement that from the immense heaps of the Swoszowice mine the sulphur can be extracted profitably with carbon bisulphide, as these heaps contain at the most only 2 per cent. of sulphur.

The Swoszowice sulphur works have two furnaces, one capable of producing 12,000 kilos. of carbon bisulphide, the other producing 7,000 kilos. per month. The yield is equal to 80 per cent.; the degree of saturation of the crude product with sulphur is less than 9 per cent., and the loss by rectification 4 per cent. The extraction of sulphur from the beds is almost complete; the residues contain only 0·5 per cent. The loss in carbon bisulphide amounts to 0·8 per cent., but will probably be reduced to 0·5 per cent. by a modification of the apparatus now in progress. D. B.

The Ammonia-soda Process in Conjunction with the Manufacture of Gas. (*Dingl. polyt. J.*, 232, 94.)—Wallace and Claus propose to pass ammonia into non-purified gas, so as to absorb the carbonic anhydride and hydrogen sulphide, the ammonia compounds thus formed being condensed in a series of scrubbers. From the last scrubber a solution of ammonium carbonate with free hydrogen sulphide is said to be obtained. This solution is either distilled and the vapours passed into a solution of salt, or it is concentrated and treated with an excess of salt, as in the ammonia-soda process. Carbonic anhydride is next passed through the solutions, sodium bicarbonate being deposited, which, after removal of the mother-liquor, is converted into the carbonate by ignition in closed vessels. The carbonic anhydride evolved serves for treating a second portion of the solution, whilst the mother-liquors are heated and treated with lime, the ammonia evolved being passed into the gas.

The following are the advantages said to be gained by this method. The cost of production of ammonium carbonate and the loss of ammonia are avoided (*i.e.*, a saving of the expense for limestone, for coals and coke as fuel). The expenses for lime necessary to decompose

the sal-ammoniac are not required. (The paper does not show how far this is the case).

The carbonic acid in the gas from one ton of coal is said to correspond with 35 to 42 kilos. of soda (100 per cent. Na_2CO_3). The Beckton Gas Works near London could accordingly produce 750 tons of soda per week, and the London Gas Companies together could produce 1,100 to 1,200 tons per week. D. B.

Superheated Steam. By L. Ramdohr (*Dingl. polyt. J.*, **232**, 67—74).—The author mentions that the use of superheated steam has not been extended as largely in industrial processes as was anticipated in the beginning, probably owing to the fact that the superheaters constructed soon become leaky and can no longer be used.

It is stated that the separate parts of the superheater should be joined without a luting, and that the tubes should be of wrought iron, and of suitable dimensions. Steam may be superheated in various degrees. Dry steam is obtained by exposing ordinary saturated steam to a temperature at which the particles of water present in the steam are subsequently converted into steam, whilst superheated steam is not merely free from these particles of water, but has a much higher temperature than saturated steam. The limit of temperature in this direction is about 600° to 700°.

Superheated steam has a larger volume than ordinary steam of the same pressure, the difference of volume being in proportion to the dégree of superheating. It is chemically indifferent to a large number of substances, and can therefore be used for evaporating solutions, distilling liquids, for the dry distillation of substances, for drying purposes, for calcining and subliming solids, &c.

The author mentions that dry or slightly superheated steam should be used whenever steam is wanted, and it is the non-observance of this maxim which annually costs millions in industrial processes. It is a well known fact that in spite of the most ingenious arrangements for economising the fuel for boilers, a large proportion of the heat is, nevertheless, unused, and escapes through the chimney. This heat could be utilised by a simple apparatus, which is placed in the flue between the boiler and the chimney. By passing the steam through this apparatus before using it, it will not merely be dried completely, but it will be superheated more or less strongly. Dry steam may be used profitably in all cases where ordinary steam is used, *e.g.*, for driving engines, locomotives, steamers, for chemical operations, &c. D. B.

Loss of Nitre in the Vitriol Manufacture. By J. Mactear (*Chem. News*, **39**, 232—234).—In the case of good plant the loss of nitre may be recognised as occurring in two ways. 1. As nitrous fumes escaping with the exit gases into the atmosphere. 2. As nitrous fumes lost in the acid run off from the chambers.

If, however, the amount of nitrous compounds capable of absorption by caustic soda in the escaping gases, and the amount of nitrous compounds in the acid used, be estimated, it will be found that these

two sources of loss are very far from accounting for the amount of nitre used.

The first series of experiments tabulated by the author gives the results of 27 weeks' working of seven series of large chambers, all worked with Gay-Lussac towers, and all but one with Glover towers, the one exception denitrating its acid by hot water in a long tunnel. The total nitre lost per week varies from 2·793 to 6·510 per cent. on the sulphur used, mean 4·569.

The nitre lost in the acid varies from 0 to 0·700 (mean 0·265), and that lost in the exit gases varies from 0·383 to 2·244 (mean 1·298) per cent. on the sulphur used.

The nitre unaccounted for by these two sources of loss varies from 2·023 to 4·311 (mean 3·016) per cent. on the sulphur used. In most cases where the percentage of nitre used on sulphur is high, so also is the loss of nitre unaccounted for.

The author has looked in three directions for sources of this loss, viz., decomposition of the nitrous gases (*a*) in contact with hot kiln gas before entering the Glover tower or chambers; (*b*) in their passage through the Glover tower; (*c*) in their passage through the condensing apparatus known as vitriol chambers.

In a series of experiments, lasting 7½ days, on vitriol chambers without Glover towers, and where all the nitre was potted in a large pot placed at the end of the row of kilns, the total nitre used was 9 per cent., and the unaccounted for loss 5·44 per cent. on the sulphur used. The Gay-Lussac tower absorbed 92 per cent. of the nitrous gases which entered it.

Using the same chambers, but substituting for the large nitre pot small pots placed actually on the burning pyrites, the seven days' experiments gave as an average, total nitre used, 11·6 per cent., and unaccounted for loss, 5·63 per cent. on the sulphur used. The Gay-Lussac tower showed an absorption of 98·8 per cent. of the nitrous gases entering it. Decomposing the nitre in small pots at a higher temperature thus results in the consumption of a considerably larger proportion of nitre, but the unaccounted for loss of nitre is not sensibly increased. Nor do the experiments cited afford any proof of a loss of nitrous compounds in the Glover towers, for whilst in the two series of experiments without Glover towers the unaccounted for loss of nitre is 5·44 and 5·63 per cent. on sulphur, in the series of experiments extending over a year, with chambers supplied with Glover towers, it is only about 3·5 per cent. J. M. H. M.

The Composition of Phosphatic Minerals. By T. Pilter (*Bied. Centr.*, 1879, 301).—This is accomplished by means of sulphurous anhydride under the pressure produced by the evolved carbonic anhydride. The tricalcium phosphate is converted into monocalcium phosphate, the calcium sulphite being separated by crystallisation. The former is either converted into superphosphate or used as a source of phosphorus. J. K. C.

Composition of a Boiler Incrustation. By A. Smetham (*Chem. News*, **39**, 236—237).—The incrustation, dried at 100° C., con-

tained—oxide of iron, 24·72; oxide of lead, 8·41; oxide of zinc, 44·39; lime, 0·99; magnesia, 0·77; sulphuric acid, 1·22; carbonic acid, 3·34; matter insoluble in aqua regia, 5·60; combined water, organic matter, and undetermined, 10·56. The boiler in which this incrustation was formed is described as a hot-water circulating boiler for domestic use, made of galvanised iron, and communicating by means of leaden pipes with a galvanised iron cylinder. The author attributes the oxidation of the iron and zinc to galvanic action set up between these metals and the lead, the latter being possibly dissolved by the boiled water from the leaden pipes, and precipitated in the boiler by the coating of zinc. The incrustation had been exposed to the air for some time before being analysed, and contained no lead in the metallic state.

J. M. H. M.

New Method of producing a Coating of Magnetic Oxide on Iron Surfaces. By G. R. Tweedie (*Chem. News*, **39**, 212).—In the course of experiments with Bower's process for coating iron with magnetic oxide by a current of hot air, it was found that the action was due to the combination of atmospheric oxygen with the carbon of the iron to form carbonic anhydride, which was then reduced by the iron according to the well-known equation, $4CO_2 + Fe_3 = Fe_3O_4 + 4CO$. Hence this process was found to be unsuitable for coating wrought iron or steel.

The mode of procedure now adopted is to heat the articles to be coated in a current of impure carbonic anhydride obtained by the combustion of small coal. By this means a coating of magnetic oxide is obtained slightly contaminated with red oxide, the conversion of which into magnetic oxide is then effected by adjusting the air supply of the furnace, so as to substitute a current of carbonic oxide for the carbonic anhydride, $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$. The coating thus produced is very hard, homogeneous, and withstands ordinary oxidising influences perfectly.

J. M. H. M.

Physical and Chemical Changes which Specular Iron undergoes, when Smelted in the Cupola for the Bessemer Process. By E. v. Köppen (*Dingl. polyt. J.*, **232**, 53—63).—Spiegeleisen is largely used in the Siemens-Martin and the Bessemer processes for re-carbonising the iron, after it has been decarbonised intentionally too far. Its action, about which there is no doubt from a practical point of view, depends theoretically not only on the large amount of carbon contained in it, but also on its peculiar character and composition. Wedding explains this action by the circumstance that the manganese contained in spiegeleisen, being oxidised readily, combines with the oxygen-bubbles present in the liquid Bessemer product, and thus imparts a greater firmness to the steel.

The specific gravity of white pig-iron varies from 7·056 to 7·889. The author found that the presence of manganese in specular iron considerably alters the specific gravity. It was shown that the specific gravity of the metal was less after smelting in the cupola than before, the decrease in manganese also diminishing the specific gravity.

According to Mayrhofer, the specific heat of spiegeleisen is 0·1182 and 0·1197 (*i.e.*, more than the specific heat of the other kinds of pig

iron, which vary between 0·1176 to 0·1182). Bolley and Stölzel give 0·1138, and Wedding 0·11284 and 0·11398. No changes were noticed after smelting spiegeleisen in regard to its specific heat.

As to the colour and lustre which characterise spiegeleisen, it was found, that when smelted, the metal assumes a white, dull appearance. The crystalline form, texture, and grain also change during the smelting operations; the hardness and brittleness are much altered. After smelting, spiegeleisen fails to scratch glass and loses its property of shivering to pieces when broken up. The firmness does not appear to be altered. With regard to the chemical changes which take place, when spiegeleisen is heated in the cupola furnace, it was found that the quantity of silica, carbon, and phosphorus originally present was increased, a circumstance which is due to the oxidation of iron and manganese, the original quantities of silica, carbon, and phosphorus being spread over a smaller quantity of material. A decided decrease in manganese was noticed, which amounted to one-fifth to one-third of the total quantity present. The smelted metal had absorbed a trace of sulphur from the pyrites contained in the fuel used. The original metal was perfectly free from sulphur. These changes seem to indicate that spiegeleisen can be used with great advantage in the above process, as they are too insignificant to interfere with the success of the operation. Moreover, on account of the saving in fuel and the fact that in the old puddling process more sulphur was introduced into the smelted metal, the cupola furnace is to be recommended. D. B.

Combustion in the Blast Furnace. By J. A. Church (*Dingl. polyt. J.*, **232**, 83—86).—It is a well-known fact, that under similar conditions a ton of pig-iron can be made with less fuel when charcoal is used than when coke or anthracite is the heating material. Various theories have been drawn up to explain the cause of this superiority. Charcoal possesses the property of reducing the carbonic acid formed in the combustion, quickly and completely to carbonic oxide. This property belongs to charcoal in virtue of its porous structure. According to this theory, therefore, the carbonic acid formed by the action of the air upon the fuel is immediately reduced in charcoal furnaces to oxide, and the gas reaches its highest reducing power even in close vicinity to the tuyeres. The practical man, however, attributes the superiority of charcoal to the fact, that the comparatively large consumption of dense fuels depends to some extent on their slower rate of combustion.

In order to explain this action correctly, it is necessary to consider this subject from another point of view. It has been proved that anthracite furnaces use much more coal than charcoal stacks, even when working under almost similar conditions. It would seem, therefore, that the superiority of charcoal depends on the difference in the igniting powers of the three fuels mentioned, and the author, in rejecting the above theories, mentions that the highest carbon duty is given by a fuel which withdraws the most oxygen from the blast in a given space of time. The proportion of oxygen in the air is a very important point in this matter. The igniting power of carbon varies

decidedly with the nature of the fuel. Charcoal is most easily ignited, a match or a few shavings being sufficient to set it in combustion. Anthracite, however, requires a mass of live coals, or the flame of a considerable quantity of wood for its ignition. Even with a fuel so easily ignited as a candle, the flame ceases, when a few per cent. of carbonic acid is present. This loss of igniting power can only be attributed to the supposition that the carbonic acid acts as an inert substance, replacing the same quantity of oxygen. It would seem, therefore, that light charcoal forms the best fuel for blast furnaces, and the reason that its use has not been applied profitably in furnace work is probably due to the fact, that porous coke is generally contaminated with slate. If, however, it were possible to prepare a light fuel cheaply and of the necessary degree of purity, a great financial result in the blast-furnace industry would be attained. D. B.

Third Form of Carbon in Steel. By H. G. Debrunner (*Dingl. polyt. J.*, **231**, 475, and *Iron*, **12**, 775).—When homogeneous (crucible or Bessemer) steel is dissolved in nitric acid of 1·2 sp. gr., there appears in the solution a brown flaky deposit, which disappears on heating. If, on the contrary, graphite or uncombined carbon is present, the flakes remain undissolved even after warming for several hours in a water bath, and they are affected neither by alcohol nor by alkalis. On treating welding steel (puddle steel, blister or cement steel) with nitric acid as described above, there forms in the greenish solution at the bottom of the vessel a velvety black powder, which resembles graphite in appearance, but is completely dissolved on heating. These phenomena induced the author to undertake a research into the subject, from which he has been led to the conclusion that carbon is present in iron in three distinct forms, the first two being the chemically combined carbon and the carbon as graphite, and the third which he has discovered he terms "half-combined carbon." A consideration of the relative quantities of these forms of carbon in any sample of iron will give a good idea of the method by which it has been manufactured. For instance, hot-blast coke pig-iron contains as much graphite as there is of both combined and half-combined carbon, whilst the last-mentioned is present in smallest proportion.

Again, in the case of cold-blast wood-charcoal pig-iron, the half-combined iron exists in largest proportion, and this, together with the chemically combined carbon, exceeds the proportion of graphite present. The quantity of silicium present is a criterion for warm or cold-blast pig-iron.

Bessemer steel, crucible steel, and steel produced in the open furnace, contain chemically combined carbon and traces of graphite, but never half-combined carbon.

Blister steel, puddle steel, and puddle iron, on the contrary, contain half-combined carbon, part of which is transformed into chemically combined carbon, on hammering into rods and plates. W. T.

Beer Analyses. (*Bied. Centr.*, 1879, 201—203).—H. Brackebusch.—Mean results of 27 samples of sedimentary fermented Berlin beer:—Alcohol, 4·74 per cent. (max. 5·4; min. 3·6). Extract, 4·94 per cent.

(max. 6·13; min. 4·0). Malt sugar, 3·78 per cent. (max. 4·5; min. 2·55).

F. Elsner.—Mean results of 16 samples of Berlin beer:—Alcohol, 3·19 per cent. (max. 4·24; min. 1·48. This result was obtained from a white beer). Extract, 5·20 per cent. (max. 9·46; min. 3·65). Ash, 0·24 per cent. (max. 0·39; min. 0·12, from a white beer). Phosphoric acid, 0·123 per cent. max. 1·0; min. 0·052). Original concentration of wort, 12·23 per cent. (max. 16·6; min. 7·94 from white beer). The presence of surrogate could not be detected.

R. Fresenius and C. Neubauer.—Nassau beer:—Alcohol, 3·737 per cent. Free carbonic acid, 0·285 per cent. Extract, 6·035 per cent. The extract contained—phosphoric acid, 0·072; potash, 0·082.

No foreign bitter principle was found.

Mean results of 20 samples of Hanoverian Beer (a), and of Beer from various sources (b):—

Sp. gr. at 17·5°.	100 parts of the beer freed from CO_2 contained.			Extract contained.		Phosphoric acid in ash.	Original concentration of wort.	CO_2.	Lactic acid.
	Water.	Alcohol.	Extract.	Organic.	Fixed.				
(*a*) 1·0165 ...	89·64	4·01	6·34	6·10	0·24	0·069	14·36	—	—
Max. 1·0353 ...	91·61	5·05	13·91	13·65	0·28	0·093	17·37	—	—
Min. 1·0115 ...	85·37	0·72	4·43	4·15	0·19	0·042	12·33	—	—
(*b*) 1·0172 ...	89·19	4·0	6·79	6·52	0·27	0·080	14·80	0·186	0·17
Max. 1·0219 ...	90·45	5·39	8·07	7·81	0·39	0·102	18·21	0·275	0·22
Min. 1·0147 ...	86·85	3·40	5·49	5·27	0·22	0·067	13·21	0·108	0·11

None of the beers had been adulterated.

Vogel determines the phosphoric acid in beer by titration with uranium acetate, employing 100 c.c. of beer; the precipitate readily subsides on warming the solution.

Munich beer contained the following amount of phosphoric acid:—

	Per litre.
Winter beer	0·5 gram
Summer beer	0·6 „
Strong ale	0·9 „

A. J. C.

Preparation of Pressed Yeast as a Bye-product from Potato Spirit. By A. Stutzer (*Bied. Centr.*, 1879, 220—224).—The author describes in detail a process by which pressed yeast can be obtained as a bye-product in the preparation of potato spirit. Further experiments are, however, required before it can be profitably worked, as when the operation was conducted with the two-fold object of obtaining spirit and yeast, the yield of spirit was always less than it should have been.

A. J. C.

Artificial Animal Charcoal. By J. Pilter (*Bied. Centr.*, 1879, 198—199).—Leather waste is heated under a pressure of six atmospheres, with a solution containing 1—5 per cent. by weight of caustic soda. The gelatin is obtained from the pulp by means of a centrifugal machine, and so much as equals 33 kilos. of dry glue is mixed with 50 kilos. of bicalcium phosphate and 17 kilos. of magnesium phosphate. The tolerably dry mixture is subjected to hydraulic pressure, which gives it a bone texture, then dried at 110°, and calcined in the usual manner. The composition of the material can be varied according to the purpose to which the charcoal is to be applied. A. J. C.

Purification of Beet-root Syrup. By F. Pokorny (*Bied. Centr.*, 1879, 298—300).—This the author endeavours to accomplish by means of tribasic ammonium phosphate and caustic baryta, and finds that it succeeds better than the older methods. The composition of the precipitate thus obtained shows that it would be valuable as a manure.

J. K. C.

Recovery of Sugar from Molasses. By Steffens, Manoury, Mateyczek, and Drevermann (*Bied. Centr.*, 1879, 296—298).—The sugar is precipitated from a dilute solution of molasses by milk of lime, which carries down about two-thirds of the sugar. The precipitate is filtered, pressed, and used instead of lime in the preparation of sugar; the filtrate is used to dilute the molasses for a fresh precipitate. Drevermann decomposes the sugar-lime with sulphate of magnesia.

J. K. C.

Studies on the Crystallisation of Sugar and on the Preparation of Sugar-candy. By M. Weitz (*Dingl. polyt. J.*, **231**, 452).—Although the preparation of sugar-candy, especially in northern France and Belgium, has acquired a great importance, still it has been little studied. Large quantities of uncrystallised sugar are produced by manufacturers owing to a want of knowledge of the conditions necessary to produce the crystalline product.

According to the process usually adopted, the raw sugar solution is first purified in the usual way and then concentrated either in a vacuum or in the open air, until it indicates from 38° to 41°. Usually this mass boils at about 110° to 120°, and 1 litre at 15° weighs from 1,420 to 1,450 grams.

For the purpose of crystallisation, copper vessels, in the form of truncated cones, are employed, through minute holes in the walls of which threads are passed by means of needles, the holes being then stopped up with paper or clay paste. Each vessel contains generally from 19 to 20 kilos. of syrup, but in some districts the vessels are made much larger.

The chambers in which these pots are placed are heated with warm air, and the process of crystallisation lasts from 8 to 14 days. The vessels are then turned mouth downwards on a sieve to allow the syrup to drain away, and that which remains adhering to the crystals is then washed away with lukewarm water and the crystals are dried completely in the drying room.

In Nantes white candies especially are produced for the manufacture of champagne.

In Antwerp the work is done in a great number of small manufactories after a very primitive method, the evaporation being still carried on over the open fire. The syrup, after being clarified, is passed through Taylor's filter, then concentrated and put in pots, which are placed in a hot-air chamber to crystallise. In these manufactories the clear product of the first charge is not sought so much as the red candy of the second. By this method much uncrystallised sugar is produced. The syrup from the first crystallisation is boiled down and furnishes the desired yellow or red candy, whilst the syrup from this crystallisation, on being again concentrated furnishes a candy of a much darker colour. The syrup or molasses obtained from the third crystallisation is very sweet, and rich in uncrystallisable sugar, and is consumed in the town and neighbourhood.

The author criticises a table, made a long time ago by Dutrone, which purports to give the proportion of sugar contained in any solution as indicated by its boiling point. This table, although incorrect, is still printed in the chief works on the manufacture of sugar.

Flourens (*ibid.*, 223—275), who is accepted as the better authority, states that at 27·5° C. a saturated solution of sugar contains 67·7 per cent. of sugar and 32·2 per cent. of water, and gives a table containing practically important determinations of the yield of all syrups when cooled to any given temperature. It is of special interest to observe the small increase in the amount of sugar dissolved at the lower temperatures, so that there is no advantage in allowing the temperature to fall under 20° to 25° for white syrups and 30° for brown syrups.

If the temperature of the boiling mass reaches 130° to 140° it forms on cooling barley-sugar, as the solution is then too thick for crystals to form in it. If a portion of such a solution be stirred with a spatula when cooling, it gradually becomes thicker, and, simultaneously with throwing down sugar in the form of a powder, liberates a large quantity of steam, due, according to Dumas, to the liberation of latent heat from the barley-sugar during the process of crystallisation. According to Flourens, the warming of the crystallising vessels is not only of no advantage, but is a positive disadvantage.

As an example of the method pursued by Flourens, his first table shows the production of white candy, as manufactured from pure loaf-sugar, the percentage composition of the paste being—

Crystallisable sugar	80·00
Uncrystallisable sugar.....	traces
Ash.....	absent
Water.....	20·00
	100·00

The results given in the following table are rather higher than those obtained on the large scale, owing to the syrups remaining supersaturated:—

Duration of crystallisation.	Temperature in the vessels.	Quantity of sugar in the syrup.	Yield in candy.
		Per cent.	Per cent.
1 day	67°	78·75	5·9
2 days.....	54	76·25	15·7
3 „	45	74·25	23·0
4 „	37	72·40	27·5
5 „	33	71·50	29·8
6 „	30	70·00	33·3
7 „	29	68·50	36·5
8 „	28	68·50	36·5
9 „	28	68·50	36·5

After this follows a table showing the amounts of candy which would separate from a saturated solution of pure white loaf-sugar at different temperatures.

In the manufacture of yellow or brown candy, this second table is useless, owing to the presence of uncrystallisable sugar; and it is a strange fact that the greater proportion of uncrystallisable sugar any sample contains, the greater will be the quantity of crystallisable sugar which will be converted into the uncrystallisable variety during the process of manufacture.

For comparison with the above table the author gives another, showing the influence of the uncrystallisable sugar on the production of candy.

There are also three other tables, showing that the longer the impure sugars are kept heated in the hot air crystallising chambers the greater is the amount of crystallisable sugar which is rendered uncrystallisable. W. T.

Recent Contributions to the History of Detonating Agents. By F. A. Abel (*Chem. News*, **39**, 165—166, 177—179, 187—188, 198—200, 209—212).—In this paper the author, after briefly sketching the history of the application of the chief substitutes for gunpowder, describes the results of his own investigations on the conditions essential to the development of *detonation* in masses of nitroglycerin and gun-cotton, or preparations of them, and the relations to and behaviour towards each other of these and other explosive bodies as *detonating agents*. Not only gun-cotton, nitroglycerin, and their preparations, but all explosive compounds and mixtures, may be detonated through the agency of an initiative detonation. When induced in this way, the detonation is due not to the heat developed by the combustion of the detonating fuze, but to the mechanical force *suddenly* brought to bear on some part of the mass operated on. The action of a detonating charge on an adjacent explosive is, in fact, similar to the blow of a hammer or the impact of a projectile, and is greatest when the largest amount of force is developed in the shortest period of time by the detonating charge. The essential difference between an explosion and a detonation lies in the compara-

tive suddenness of the transformation of the explosive substance into gas or vapour.

With all explosives confinement of the charge increases the rapidity of the transformation, and tends to give it a more purely detonative character. For example, the detonation of chloride of nitrogen, although extremely violent in the open air, is rendered still more so by confinement, even beneath a thin layer of water.

The suddenness of detonation as compared with explosion is illustrated by the following experiments:—By filling a 16-pr. common shell completely with water and inserting a charge of $\frac{1}{2}$ oz. of gun-cotton fitted to a detonating fuze, the shell being thoroughly closed by a screw plug, the shell is, on firing, broken up into a number of fragments averaging fourteen times the number produced by bursting a shell of the same size with the full amount of powder which it will contain (13 oz.). Again, a charge of 5 lb. of gun-cotton or dynamite, suspended 4 feet above the centre of a plate of soft steel resting over a cavity in an iron anvil, produces, when fired by detonation, a cup-shaped indentation in the steel, the dimensions of which afford a measure of the violence of the detonation. A much larger charge of powder exploded in actual contact with the plate would produce no alteration of form, and the same negative result would accompany the *explosion* of a heap of loose gun-cotton of the same or greater weight than the charge *detonated*.

The velocity with which detonation travels along trains 30 or 40 feet in length, composed of distinct masses of gun-cotton and of dynamite, has been found by Noble's chronoscope to range from 17,000 to 24,000 feet per second. Even when spaces of half an inch intervene between the masses composing the trains, detonation is still transmitted with great though diminished velocity. An intervening space of 2 inches is, however, sufficient to prevent the communication to an adjacent heap of the detonation produced by 8 oz. of gun-cotton freely exposed. When the force is confined and directed by enclosing the charges to be detonated in tubes, detonation may be communicated through much greater distances. Thus, the detonation of a 1-oz. disk of gun-cotton in the open air cannot be relied on to cause the detonation of another disk at a greater distance than half an inch from it, but if it be just inserted into one end of an iron tube 2 feet long and 1·25 inch in diameter, a similar disk, or, even a plug of loose gun-cotton, inserted into the other extremity of the tube will invariably be detonated. With 2-oz. charges of gun-cotton in a tube of the same dimensions detonation is transmitted to a distance of 5 feet, and 2-oz. disks placed at intervals of 2 feet are detonated throughout a very considerable length of tube by the initiative detonation of the disk at one end. Detonation is also communicated through branch tubes 2 feet long at right angles to the main tube.

Experiments were made with silver fulminate in order to ascertain the influence of the material and surface texture, &c., of the tubes on the transmission of detonation. Half a grain of silver fulminate placed just inside one end of a stout glass tube 0·5 inch diameter and 3 feet long will invariably induce the detonation of a similar quantity placed just at the other end, but the result is uncertain when

the length of the tube exceeds 3 feet 3 inches. With double the quantity of fulminate, detonation can only be communicated through 31·5 inches of pewter tube, 23·7 inches of brass tube, 15·8 inches of india-rubber tube, and 11·8 inches of paper tube. The glass tubes are always destroyed by the detonation for a certain portion of their length, the pewter tubes are deeply indented, and the brass tubes are in no way injured. The sonorosity of the tube appears to have no influence on the transmission of detonation. The transmission by the glass tube is not at all affected by casing with paper or india-rubber, but is very much lessened when the inside is roughened by a coating of French chalk. Brass tubes with the inside highly polished, and paper tubes with an inside coating of highly glazed paper, transmit detonation to about the same extent as the glass tubes. The material of the tube seems therefore to have little or no influence compared with the condition of the inner surface. A diaphragm of thin bibulous paper or a light tuft of carded cotton wool, inserted midway in the glass tube, prevents the transmission of detonation even by six times the ordinary quantity of fulminate.

A remarkable want of reciprocity as regards detonation is exhibited by mercuric fulminate and gun-cotton. From 20 to 30 grains of fulminate are required to detonate gun-cotton if the fulminate is merely confined in a thin case of wood or several wrappings of paper, but as small a quantity as 2 grains of fulminate suffices if it be confined in a case of stout sheet tin tightly imbedded in the mass of gun-cotton. In attempting to communicate the detonation of the fulminate to gun-cotton through tubes, it is necessary to employ very large quantities of fulminate, even with short lengths of tube. When, however, the quantity of fulminate reaches certain limits, detonation may be communicated through very long tubes. On the other hand very much smaller quantities of gun-cotton will cause the detonation of mercuric fulminate through tubes even 7 feet long and upwards.

A similar want of reciprocity exists between gun-cotton and nitroglycerin. The detonation of $\frac{1}{4}$ oz. of gun-cotton induces the simultaneous detonation of nitroglycerin enclosed in a vessel of sheet tin at a distance of 1 inch from the gun-cotton, and with $\frac{1}{2}$ oz. of the latter detonation is produced through an intervening space of 3 inches; but on attempting to apply nitroglycerin to the detonation of gun-cotton, the quantity of the former detonated in close contact with compound gun-cotton may be increased from $\frac{3}{4}$ oz. up to 2 oz. without producing detonation of the cotton, which is simply dispersed in a fine state of division. Although gun-cotton is so much more insensible to the detonation of nitroglycerin than to that of mercuric fulminate, the force developed by the former is decidedly greater (for equal quantities) than by the latter. In like manner, although the detonation of silver fulminate is very decidedly sharper than that of the mercuric compound, yet it is in no way superior to the latter as an initial detonating agent. And although the iodide and chloride of nitrogen are far more susceptible of sudden detonation than silver fulminate, yet 5 grains of the latter, confined in a stout metal envelope, suffice to detonate gun-cotton, whilst 50 grains of chloride of nitrogen confined by water are required for the same purpose, and iodide of nitrogen

in quantities up to 100 grains fails to effect any detonation of the gun-cotton. These facts show that induced detonation cannot be due entirely to the sudden development of mechanical force and heat, and the author believes that a synchronism, or similarity of character of the vibrations caused by the detonation of two substances, favours the detonation of one by that of the other. Some experiments of Champion and Pellet also favour this view.

The physical character and mechanical condition of an explosive have great influence on its susceptibility to detonation. Liquid nitroglycerin, for example, is more sensitive to detonation than solid gun-cotton, if the mobility of the liquid be counteracted. This may be done by admixture with an inert solid, as in the case of dynamite, which is more sensitive to detonation than undiluted unconfined nitroglycerin. The rate of transmission of detonation in undiluted nitroglycerin is under 6,000 feet per second, but in dynamite it is greater than in compressed gun-cotton. Gun-cotton in a light and flocculent condition is incapable of detonation in this case as in that of unconfined liquid nitroglycerin, the sudden and violent blow which is the cause of detonation being partially consumed in producing motion in the particles of the explosive, in compressing the loose gun-cotton, and in scattering the nitroglycerin. When the force not absorbed in this way is insufficient to detonate the whole charge of explosive, detonation occurs in those portions which present the requisite conditions, and the remainder is dispersed and sometimes inflamed.

Dilution of a *solid* explosive with an inert solid greatly diminishes the susceptibility to detonation, as it practically interposes spaces between the particles of explosive. Thus a mixture of mercuric fulminate with more than one-fifth of its weight of French chalk, cannot be detonated by means of one grain of pure fulminate enclosed in a copper capsule inserted into the mixture, but the same quantity suffices to detonate undiluted fulminate through a tube 8 inches long and 0·5 inch diameter.

If, however, gun-cotton be diluted by wetting it with a *solution* of an inert salt, and compressed in the wet state, the mass when dried is nearly as sensitive to detonation as pure compressed gun-cotton, the increased rigidity conferred upon it by crystallisation of the salt almost counterbalancing the effect of the dilution. If a nitrate or chlorate be employed as the diluting agent, the mixture is quite as sensitive as undiluted gun-cotton, and is even much less indifferent to detonating nitroglycerin than the pure gun-cotton. Gun-cotton, mixed with chlorate or nitrate, is detonated with certainty by $\frac{1}{2}$ oz. of nitroglycerin, whereas 2 oz. of the latter fail to effect the detonation of ordinary compressed gun-cotton.

Gun-cotton, when diluted with an inert *liquid*, has its sensitiveness diminished much more than by dilution with a solid, the particles of explosive being completely isolated from each other by films of the liquid. Thus gun-cotton which in the dry state can be detonated by 2 grains of mercuric fulminate, is not detonated with certainty by 15 grains of fulminate if containing 5 per cent. of water (air-dried gun-cotton contains 2 per cent.).

Gun-cotton soaked in melted fat cannot be detonated by 15 grains of fulminate. 100 grains of fulminate generally fail to detonate gun-

cotton containing 10—12 per cent. of water, and 200 grains are required for gun-cotton containing 17 per cent. of water.

Wet gun-cotton is, however, more easily detonated by dry gun-cotton than by mercuric fulminate, the detonation of 100 grains of dry gun-cotton, for instance, being able to cause the detonation of gun-cotton containing 17 per cent. of water. Gun-cotton saturated with water (*i.e.*, containing 30—35 per cent.) requires 4 oz. of dry gun-cotton for detonation. The velocity with which detonation is transmitted along trains of wet gun-cotton containing about 30 per cent. of water ranges between 19,300 and 19,950 feet per second, the rate for dry gun-cotton being from 17,000 to 18,900 feet per second. The detonation of wet gun-cotton is also more violent than that of dry gun-cotton. In addition to these advantages the wet gun-cotton has that of safety in manipulation. If it contains 15 per cent. of water, it may be thrown on to a fire or held in a flame without exhibiting any tendency to burn; and masses of it may be perforated by a red-hot iron or with a drilling tool, or cut into slices by saws revolving with great rapidity. In one of the experiments described 20 cwt. of wet gun-cotton was packed in cases placed in a magazine, and then surrounded with a fire; in less than two hours the whole of the gun-cotton had burned away without any approach to explosive action. Various attempts have been made to use gun-cotton as a vehicle for nitroglycerin. *Glyoxilin*, consisting of gun-cotton saturated with nitroglycerin, contains a considerably smaller proportion of the latter than dynamite; but the absorbent itself being a highly explosive body the explosive power of the mixture is about equal to that of dynamite. Noble discovered that nitroglycerin exercises a solvent action on the gun-cottons which are less explosive than tri-nitro-cellulose (collodion pyroxilin). On macerating 7—10 per cent. soluble gun-cotton with 93—90 per cent. nitroglycerin the mixture becomes a gelatinous or gummy mass, from which the nitroglycerin is with difficulty separated even by prolonged immersion in water. This *blasting gelatin*, as Noble has called it, is a more powerful explosive than dynamite, or than a mixture of nitroglycerin with the most explosive gun-cotton. Moreover, since nitroglycerin contains a slight excess of oxygen over that needed for complete oxidation, whilst the soluble gun-cotton contains scarcely enough for this purpose, a mixture of the two would be expected to be slightly more powerful even than pure nitroglycerin. This is found by experiment to be the case, but unless the blasting gelatin be strongly confined, it requires a much larger detonating charge than dynamite or other solid preparations of nitroglycerin. If charges of compressed gun-cotton, compressed nitrated gun-cotton (tonite), blasting gelatin, and dynamite, be detonated upon the surfaces of a series of iron plates, the greatest indentation is produced by the compressed gun-cotton, the next greatest by tonite, then dynamite, and the smallest by blasting gelatin. But if rigidity be conferred upon the blasting gelatin by freezing, it produces an indentation greater than that produced by the compressed gun-cotton. Similar results are obtained by exploding the various charges at the bottom of cylindrical cavites in heavy leaden blocks.

If 10 per cent. of the most explosive gun-cotton be mixed with

blasting gelatin, it renders the mixture very much more sensitive to detonation by the increased rigidity which it confers upon it, whilst the explosive power is not diminished. The addition of certain substances rich in carbon and hydrogen, and soluble in nitroglycerin, such as benzene, nitrobenzene, and camphor, to the blasting gelatin, very considerably reduces its sensitiveness to detonation by the impact of bullets, and attempts have been made to render its transport and manipulation safe by this method. The camphoretted gelatin, however, still remains inflammable, and is liable to violent explosion if burned in bulk, and it requires an inconveniently large and powerful detonating charge to ensure its detonation when wanted. The camphoretted gelatin appears to be unalterable under water, and it has been proposed to render its storage safe by taking advantage of this fact. Although preparations of nitroglycerin in the frozen condition detonate more violently than when plastic, yet they are not so easily detonated by a blow or an initiatory detonation. On the other hand, if subjected to the rapid application of great heat, as by setting a portion on fire, detonation is much more readily brought about in the frozen than in the plastic material. For example, 50lbs. of plastic dynamite cartridges will burn away without explosion, but on setting fire to only 15lbs. of frozen dynamite a very violent detonation takes place when part of the material has been burned away. The author explains this by supposing that the freezing takes place irregularly throughout the mass, certain softer portions becoming enclosed in hard frozen crusts, which act like metal envelopes in promoting the detonation of their contents.

Reduction of temperature has no effect on the susceptibility to detonation of dry gun-cotton, but *wet* gun-cotton when frozen has its sensitiveness greatly increased. Wet gun-cotton containing 10—12 per cent. of water requires 100 grains of fulminate for detonation, and if containing 15—17 per cent. water it requires 200 grains; in the frozen conditions, these two qualities of gun-cotton can be detonated with 15 and 30 grains of fulminate respectively. The temperature of explosion of gun-cotton is about 4400° C., more than double that of gunpowder; the tension of the products of combustion, assuming the material to fill entirely the space in which it is fired, is considerably more than double that of the powder products under the same conditions. The products of detonation of gun-cotton are comparatively simple and very uniform under different conditions as regards pressure.

J. M. H. M.

Examination of Chinese Tea. By Eder (*Dingl. polyt. J.*, **231**, 445—451, and 526—532).—The adulteration of tea is as common as that of wine, and as difficult to detect even by the educated taste.

It is a constant practice to mix old teas with those which have been newly plucked, and the worse with the better sorts, and to call them by fancy names.

"Scenting" may be regarded as a kind of falsification; this is done by laying in contact with the tea, strong smelling flowers such as roses, jasmine, orange, olives: the chemical or dietetic value of the tea, however, is not altered by this treatment.

The materials by which tea is adulterated may be divided into four groups:—

(1.) *Mineral substances* for increasing the weight; these are never used except for the very cheap sorts, and never in the sorts which consist of recognisable leaves or of fragments of leaves.

(2.) *Mineral colouring materials*, such as salts of copper, for giving a green colour to the leaves, were never found by the author, and he found Prussian blue only in one instance. The colouring of green tea seems at present to be seldom practised, but colouring matter, if present, can be readily detected by shaking the tea with cold water, and examining the residue which settles to the bottom.

(3.) *Organic substances* for the purpose of increasing the weight, among which may be mentioned, the leaves of other plants and exhausted tea leaves.

(4.) *Organic colouring matters and Astringents*, such as tannin extracts.

The last two modes of adulteration are the most common. As much as 5 per cent. of the leaves of the willow and the sloe, which, when dried, closely resemble the leaves of green tea, are often found, but the leaves of the rose, strawberry, ash, white-thorn, poplar, mountain-ash, buckthorn, and the cornel are often employed. This mode of adulteration can be detected by infusing a small quantity of the leaves in warm water, spreading them out and examining them botanically. About 200 substitutes are used for mixing with Chinese tea. The author has never found the best teas in Austria to be adulterated, but the supply of exhausted leaves in large towns for mixing with the cheaper kinds of tea is a regular trade. Out of five samples of tea bought in the suburbs of Vienna from small shops, three had been mixed with exhausted tea leaves, and one of them had besides been adulterated with catechu.

The detection of these adulterations is very difficult; the estimation of theine furnishes no criterion, as the amount varies much in genuine teas. The author relies principally on the following four determinations:—

1st, proportion of extract in hot water.
2nd, „ tannin in the decoction.
3rd, „ ash.
4th, „ soluble and insoluble matter in water, contained in the ash.

The author's method of analysis is to take 2 grams of the tea and digest it four times successively with about 100 c.c. of water each time for half an hour to an hour; the insoluble matter is then collected and weighed on a tared filter after being allowed to dry in the air during several days.

In the filtrate the tannin is determined by the author's copper acetate method (this Journal, vol. **34**, p. 918).

For ash, he incinerates at least 2 grams; moistens the ash with ammonium carbonate solution, and after gently heating, weighs. The ash is then digested with water, the solution is filtered, and the insoluble matter weighed: the difference gives the proportion of soluble matter.

For comparison the author selected and analysed samples of different kinds of tea which he was satisfied were free from adulteration, and after infusing part of each of these samples in water in the usual way,

he dried and submitted them to analysis for comparison, and obtained the following results for the various individual samples.

Designation of the kind of Tea leaf.	Percentage.							
	Original leaves.				Leaves once infused.			
	Tannin.	Extract soluble in water.	Total ash.	Ash soluble in water.	Tannin.	Extract soluble in water.	Total ash.	Ash soluble in water.
Black Congo, No. 1	11·20	40·30	5·43	2·83	4·14	10·20	3·92	0·94
„ „ No. 2	10·10	39·40	6·21	1·55	5·65	15·30	4·80	0·46
„ „ No. 3	8·36	37·60	6·05	2·32	3·31	8·50	4·27	0·39
„ Kaisow Congo ...	9·28	37·50	5·39	1·98	—	—	—	—
„ Moning „ ...	11·32	39·90	5·03	3·03	3·73	12·90	3·88	1·27
„ Congo (ordinary).	8·24	31·70	6·12	2·73	—	—	—	—
„ Souchong, No. 1..	8·16	34·40	5·27	2·90	2·51	12·40	—	—
„ Assam Souchong.	10·95	44·30	5·22	3·09	5·07	19·70	4·96	1·05
„ Peko bloom tea, No. 2	11·76	42·70	4·98	3·10	—	—	—	—
Green Haysau, No. 1 ..	12·44	43·20	4·89	2·77	5·36	13·20	3·41	0·74
„ gunpowder, No. 1	12·43	39·60	5·09	2·76	—	—	—	—
Yellow Japan tea	13·07	39·50	5·81	2·73	2·62	12·00	3·40	0·47

From analyses of a number of samples of different kinds of tea, the author has taken the following as representing the composition of each :—

Designation.	Percentage.			
	Tannin.	Extract soluble in water.	Total ash.	Ash soluble in water.
Black tea. Souchong and Pouchang.....	9·18	38·30	5·88	2·85
Black tea. Congo	9·75	37·70	5·70	2·41
Black tea. Bloom tea.....	11·34	40·00	5·27	2·59
Yellow tea.....	12·66	40·80	5·68	2·64
Green tea (Haysau and gunpowder).....	12·14	41·80	5·79	2·95
Black tea (average of 25 samples)	10·09	38·70	5·62	2·75
Yellow and green tea (average of 9 samples)	12·40	41·30	5·73	2·79

On comparing the analytical results with those given in most handbooks, the author finds that the percentage of tannin given is usually too high, whilst the average amount of extractive matter soluble in water is higher than that given by Wigner, in the proportion of 40 per cent. as against 31·35 per cent.

Good tea must, therefore, contain:—

(1.) Not less than 30 per cent. of extractive matter soluble in water, which is also the minimum amount allowed by the English law.

(2.) At least 7·5 per cent. of tannin.

(3.) Not more than 6·4 per cent. of ash.

(4.) Not less than 2 per cent. of ash soluble in water (the English law requires 3 per cent., but the author never found so large an amount).

The presence of colouring matters, such as catechu, may be shown by the peculiar colour of the solution, and by its becoming turbid on cooling, from precipitation of catechu; but this last is not a sufficient criterion, because strong infusions of many kinds of genuine tea, such as Assam, Peko, Souchong, also become turbid on cooling, in consequence of the separation of tannate of theïn.

A good test for *catechu* is to make decoctions of 1 gram of a good tea in comparison with 1 gram of the suspected sample, boil each solution with excess of sugar of lead, and filter. To the filtrates (which should be colourless) a solution of silver nitrate is added. If the tea contain catechu, it will produce a copious flaky precipitate of a yellow-brown colour, whereas if it do not, only a slight greyish-yellow turbidity will be formed.

Test for Logwood.—The tea is steeped in cold water, whereupon if logwood is present, the blackish solution which results is changed to a bright green by the addition of a little sulphuric acid. Another delicate test for logwood is the addition of a solution of yellow chromate of potash to the cold aqueous infusion of the tea; if logwood be present, a blackish-blue colour will be produced, whilst if the tea be pure it will have no effect.

Iron salts, which may be added as colouring materials, may be detected by estimating the proportion of iron in the ash. Pure tea contains from 0·03 to 0·12 per cent.

The author found only four sorts of adulterated tea, and the following table gives the results which enabled him to arrive at that conclusion.

Designation.	Per cent.			
	Tannin.	Extractive soluble in water.	Total ash.	Ash soluble in water.
Russian tea (probably Souchong)	6·60	18·4	4·76	0·85
Bloom tea (Blüthen-thee)	4·91	15·3	3·34	0·54
Bloom tea (Blüthen-thee)	5·13	14·6	4·51	0·90
Black tea (probably Souchong)..	19·77	22·4	3·07	1·12

The first three samples were adulterated with exhausted leaves, whilst the last contained a tannin material, which was proved by the tests above mentioned to be catechu.

For the purpose of recognising and classifying the different teas of commerce, the author tried to determine the characteristic external features of the most important kinds, and divided them into four chief groups:—

(1.) *The hairy black, i.e.*, the so-called bloom tea (Peko tea), whose upper surface is darkish, whilst the under surface is covered with silvery hairs which can be seen by the naked eye. The leaves are about 3 or 4 cm. long and 1 cm. broad, but there are also mixed with it many young leaves and even twig-ends. The Assam Peko has a shorter and broader leaf than the China. The former has a strong but not less fine aroma than the latter, and gives a darker infusion.

(2.) *The smooth black tea* has no silvery hairs. In this group many varieties are included, among which may be mentioned the Congo and Souchong; these two sorts are difficult to distinguish from each other. Souchong consists of full grown leaves from 5 to 6 cm. long and 2 to $2\frac{1}{2}$ cm. broad, which are brownish, very slightly haired underneath, and for the most part with their points broken off.

Congo shows more of a reddish-brown colour, especially in individual leaves. The leaves are from 3 to 7 cm. long and 2 cm. broad. In Congo as in Souchong many young leaves are to be found.

Pouchong is a very large-leaved tea, the average being from 8 to 9 cm.

(3.) *Yellow teas.—Oolong tea* is externally not very different from black tea, and only a fragment of the leaves shows the characteristic of yellowish-brown colour.

It is an interesting fact that when these leaves have been extracted with hot water and are still wet, they appear green, and from this they can be readily distinguished from black tea.

The author could obtain only two sorts of yellow tea. The yellow Japan and the Oolong-Mandarin, both of which were of similar dimensions, viz. from 3 to 4·5 cm. long and 1·5 to 2 cm. broad.

(4.) *Green teas* are readily distinguished by their colour.

Haysam leaves are cylindrically twisted.

Pearl tea (gunpowder-tea) is found in well-shaped rolled-up pellets, and this class may be further subdivided in accordance with the size of the pellets.

The Chinese alone distinguish more than 700 varieties.

The amounts of other ingredients occurring in tea were determined. Moisture found by drying at 100° varied from 5 to 14 per cent. The tea oil was determined by distilling 200 grams of tea with $1\frac{1}{2}$ litres of water: the oil was taken up by ether from the distillate, and the ether afterwards separated from it by distillation. Peko bloom tea gave 0·41 per cent., and gunpowder-tea gave 0·52 per cent.

The oil is bright yellow, but darkens in colour and becomes resinous on exposure to the air for a few days. It turns reddish-brown with nitric acid. After the watery distillate has been exposed for some time to the air, it loses its aromatic smell and little or no oil can then be separated from it by ether, the whole having been transformed

into a resinous substance; and even if the distillate be kept in closed vessels, the aroma is soon lost. It is therefore supposed that tea-leaves by age lose their aroma in consequence of the tea oil being converted into a resinous matter.

The theine obtained amounted to 2 per cent. Of the 40 per cent. of extractive matter found by the author, from 15 to 16 per cent. was insoluble in strong alcohol, about 12 per cent. was albuminous matter, probably legumin, which was estimated by Toller's nitrogen process, and the remainder consisted of gummy matters, sugar, dextrin, and colouring matters.

Chlorophyll, fat, resin, &c., were extracted with ether from the insoluble matter, and Peko tea was found to contain about 7 per cent. of these substances. The remaining cellulose was purified by digesting alternately with nitric acid, potash, and alcohol.

The following table shows the average composition per cent. of tea:—

A. *Soluble in Water: 40 per cent. Organic Matters.*—Hygroscopic water, 10·0 per cent.; tannin, 10·0; gallic acid, oxalic acid, and quercetin, 0·2; boheic acid, 0·1; theine, 2·0; tea oil, 0·6; albuminous bodies, probably legumin, 12·0; gummy substances with dextrin and sugar, 3 to 4.

Mineral Matters, 1·7.—Composed of: K_2O, 0·938; Na_2O, 0·014; CaO, 0·036; MgO, 0·051; Fe_2O_3, 0·024; Mn_3O_4, trace; P_2O_5, 0·133; SO_3, trace; SiO_2, 0·021; CO_2, 0·430; Cl, trace.

B. *Insoluble in Water: 60 per cent. — Organic Matters.*—Albuminous bodies, 12·7 per cent.

Ethereal Extractive.—Chlorophyll, 1·8 to 2·2; wax, 0·2; resin, 3·0; colouring matter, 1·8. Extractive matter for the most part soluble in nitric acid, 16·0; cellulose, 20·0.

Mineral Matters, 4·0.—Composed of: K_2O, 0·290; Na_2O, 0·052; CaO, 0·584; MgO, 0·592; Fe_2O_3, 0·045; Mn_3O_4, 0·019; P_2O_5, 1·031; SO_3, 0·046; SiO_2, 0·680; CO_2, 0·744; Cl, trace. W. T.

Composition of Skimmed Whey. By L. Manetti and G. Musso (*Landw. Versuchs.-Stat.*, **23**, 429—436).—The authors define skimmed whey as the liquid remaining after the removal of the sweet and acid deposits from whey (*Mascarpa dolce and Mascarpa acida*) by means of boiling and fermentation. In Lombardy these deposits are of great practical value, not only because of their nutritive qualities, but also in their application to the determination of the character of the cheese which has been separated from the whey, the relative quantity of acid and sweet deposit affording the cheesemaker a criterion as to how the preparation will succeed. The objects which the authors had in view in undertaking the analysis of skimmed whey, were to observe the changes which the milk had undergone during the process of the removal of cheese and the sweet and sour acid deposits, and also to ascertain the nutritive qualities of skimmed whey. In the analyses given below the constituents were determined in the ordinary way:—

	I.		II.	
	Milk.	Skimmed whey.	Milk.	Skimmed whey.
Water	88·930	93·352	89·052	93·971
Solids	11·070	6·648	10·948	6·029
Nitrogen	0·580	0·059	0·597	0·064
Sugar	4·979	5·176	4·633	4·770
Lactic acid	0·109	0·198	0·080	0·096
Fat	2·026	0·026	1·763	0·042
Ash	0·736	0·570	0·768	0·592
Potash	21·697	32·991	25·191	33·948
Soda	9·211	13·895	7·424	13·316
Lime	27·181	16·710	25·771	20·310
Magnesia	2·349	0·451	2·129	0·374
Ferric oxide	0·433	0·132	1·382	0·145
Sulphuric andydride	2·169	1·246	2·243	1·469
Phosphoric anhydride	26·210	18·810	25·249	15·306
Chlorine	11·101	15·946	10·165	15·447
Total	100·351	99·994	100·185	100·335
Carbonic acid	4·030	6·106	4·778	2·829

The nitrogen in the above cannot be reckoned as proteïn, because in whey nitrogenous bodies occur which do not belong to the albuminoïd series. It will be noticed that skimmed whey contains about one-seventh the quantity of nitrogen contained in milk. The cause of the relatively larger amount of sugar in skimmed whey arises from the loss of volume by boiling which the milk undergoes during the process of conversion, in which of course lactic acid is formed. The small quantity of fat is due to the presence of small flocks of the deposits before mentioned, which cannot be entirely got rid of by filtration. The quantity of ash present is about three-fourths of that in milk, some of the phosphates having been removed along with the curds, while on the other hand salt is introduced with the rennet. The earthy phosphates are probably held in solution by the lactic acid and nitrogenous compounds present.

The authors regard skimmed whey as milk deprived of its colloïd constituents, and consider its nutritive power as about one-tenth of that of milk. J. K. C.

Alpine Dairy Process. By W. Eugling and v. Klenze (*Bied. Centr.*, 1879, 204—210).—The quantity of produce which was daily obtained per cow during the year 1877, whilst the cows were pasture-grazing at Furx, near Feldkirch, for about 120 days, is as follows:—

Milk (kilo.).	Butter (kilo.).	Cheese (kilo.).
8·6	0·82	0·50

The average composition of the produce is shown as under—

	Water p. c.	Fat p. c.	Caseïn p. c.	Milk-sugar p. c.	Ash p. c.	Specific gravity. Unskimmed.	Specific gravity. Skimmed.	Cream p. c.
Milk :—						1032		
Mean.....	87·190	4·018	2·757	5·238	0·794	1080·4	1034·8	12
Minimum....	96·550	3·723	2·652	5·072	0·728	1029·4	1033·2	11
Maximum....	87·725	5·045	2·972	5·679	0·892	1031·9	1036·2	13

see errata p. 1168

Butter analysis is not given in this paper, which is an abstract of the original.

		Fat.	Caseïn.	Milk-sugar.	Ash.
Cheese :—					
Produced from equal parts of fresh milk, and milk which had been skimmed after 12 hours' standing.	mean ...	24·08	22·71	2·63	2·87
	min.....	20·52	21·23	2·25	2·71
	max.....	29·12	23·48	3·08	3·14
Skimmed cheese :—					
Produced from equal parts of milk which had been skimmed after standing 24 hours and 36 hours respectively.	mean ...	12·17	31·08	2·76	3·79
	min.....	10·08	29·14	2·11	3·10
	max. ...	13·21	33·63	3·43	3·88
Butter milk.....	mean ...	1·023	4·942	4·785	0·881
Curd.....	,,	3·736	18·557 Lactoprotein, &c.	3·918	2·161
Whey.....	,,	0·093	0·305	5·599	0·391

see errata p. 1168

An investigation was made as to the effect of the quantity and composition of the milk yielded by cows grazed on pasture land which had been manured with the view of increasing the supply of fodder. In composition and in quantity it was practically identical with milk obtained from cows which had grazed on the unmanured pastures.

Mountain-made butter decomposes more quickly when kept in the valleys than it does on the mountains. This is attributed to the large quantity of ozone which was found to be present in the atmosphere of the valleys, as according to the authors' experiments, ozonised air decomposes butter very rapidly.

Against this supposition of the authors as to the agency of ozone in decomposing butter, must be considered Pasteur's observations that the atmosphere of the mountains is more free from sporadic germs than that of the valley. A. J. C.

Ripening and Decomposition of Cheese. By E. Duclaux (*Bied. Centr.*, **8**, 218—220).—The curd is obtained from milk in the usual manner, and in the Salers cheese consists of caseïn, 25 per cent.; butter, 25 per cent.; whey, 50 per cent., containing about 4 per cent. of milk-sugar, which is strongly retained by the curd. After some days the curd begins to ferment, alcohol, acetic acid, and 1—5 per cent. lactic acid being formed. The yellow mass is now sprinkled with salt and pressed to get rid of water and fungous growth.

The pressed cheese in then placed in cellars to gradually ripen and to acquire its piquant flavour. It is at this stage that the caseïn is gradually transformed into soluble albuminoïds, and that the cheese is in danger of becoming rotten before it has fully ripened. In this latter case the caseïn is decomposed into leucine, "soluble albumin," and ammonia. The so-called soluble albumin has a rotatory power of −38°, and appears to be of the nature of a peptone. As the decomposition in the cheese proceeds, the albumin is gradually converted in this soluble form.

In some instances of decomposition, the author has found as much as 0·3 per cent. of valeric acid and 0·05 per cent. of acetic and butyric acids respectively.

The following analyses are of sound and decomposed cheeses:—

	Sound cheese. Salers.	Decomposed cheese. Salers.
Water	44·8	40·0
Fat	22·5	30·0
Caseïn	12·4	19·0
Albumin	10·6	2·8
Substance soluble in water	7·5	7·1
Salt	2·2	1·1
	100·0	100·0

The decomposition of cheese in this manner is ascribed to the milk-sugar in the whey, of which too much has been left in the curd.

A. J. C.

Conversion of Rags and Hair into Manure. By L. Riess-müller and H. Wiesinger (*Bied. Centr.*, 1879, 302).—These are first boiled with lime: after drying, the nitrogenous constituents are separated in a powdery state by mechanical means, cellulose remaining behind.

J. K. C.

Strength of Hemp. By F. Haberlandt (*Bied. Centr.*, 1879, 307).—A hemp cord of one square millimeter section will bear on the average 34·5 kilos. and occasionally as much as 50 kilos. Hemp is not very elastic; it is only capable of extension to the amount of 1·3 per cent. of its length.

J. K. C.

Fibrous Materials. By J. Moeller (*Dingl. polyt. J.*, **231**, 463).—The author considers that the endeavours to increase the numbers of useful fibres has not been followed by satisfactory results, although

during the last ten years we have been made acquainted with hundreds from different sources. Most of these have been rejected on theoretical grounds, a few have been tested practically, and only one, which had been used extensively in India for a long time, viz., jute, has been made available in European industry.

The fibres obtained from the following plants the author has examined by the microscope, and having also tested them in other ways, he considers them worthy of being recommended to further notice.

Lagetta furiofera.—This plant is related to our Spurge-olive, its stem, bark, and raw separated fibres have been brought from Guadaloupe. It has a round stem about 1 cm. thick, and is covered with a bark 0·3 mm. thick. In the inner bark the bast-fibres form quantitatively the most important part of the plant. The fibres are bright-coloured and of great fineness and beauty, and under the microscope are seen to split up into their primitive elements, the bast-fibres, which are from 0·03 to 0·06 mm. broad, and of extraordinary length, often spiral and finely pointed. This fibre is at present used in the manufacture of paper.

Pipturus argenteus.—Several kinds of pipturus are called in Tahiti by the name "Roa." They grow wild in the islands of the Pacific in large quantities. From their fibres are made rope-ware and sundry articles of luxury. Near relations of these nettle-like plants supply China grass. Samples in the different stages of preparation were shown at the last Paris exhibition, and testified to the ease with which this raw material can be made into fine fibres fit for spinning. The fibres have a rich silky appearance, although they are not specially pliable. The individual fibres have a mean breadth of ·025 mm., and resemble flax. They swell up to a marked extent and unequally, when placed in ammonio-oxide of copper, and they are coloured rose-red by chloriodide of zinc.

Artocarpus speciosus.—It is known that the bast (inner bark) of the bread fruit tree forms rope-wares, and serves the aborigines of the South Sea Islands for clothing. A piece of stuff several square meters in size, very like ordinary flannel in appearance, was amongst the exhibits from Tahiti at the Paris exhibition. It was probably prepared by steeping, beating, and bleaching the bark, and consists of bast fibres in several sheaths and loosely felted, with which are mixed up remnants of a thin walled tissue. They are almost completely free from woody formation, swell up in ammonio-oxide of copper as rapidly as cotton, with formation of blebs in the walls. As the trees are widely cultivated for their fruit and timber, large quantities of this fibre can be obtained.

Tacca pinnatifida.—The author recommends the leaves of this plant, called "pia" in Tahiti, as a source of raw material, from their fineness, beautiful colour, and agreeable gloss. These leaves are more than a meter in length, and several centimeters in breadth, and they readily split up along the parallel leaf-nerves, which are 2 or 3 mm. apart from each other. Microscopic examination shows layers of thin-walled parenchyma-cells, accompanying the bast fibres. They are much lignified, and are coloured dodder-yellow by aniline-sulphate. W. T.

General and Physical Chemistry.

Ultra-violet Limit of the Solar Spectrum. By A. Cornu (*Compt. rend.*, **88**, 1101—1108).—The apparatus used in the researches to which the present paper refers was described in a former communication (*ibid.*, **88**, 104). The results were influenced by the state of the atmosphere, the altitude of the sun, or thickness of the stratum of air through which the solar rays passed, and to a certain extent, by the photographic processes employed. The extreme limit of refrangibility observed corresponded with a wave-length of 293. The author believes that this limit depends on the absorptive power of the atmosphere for the more refrangible radiations, and that probably it will not be surpassed, except perhaps in observations made at a great altitude above the sea level. R. R.

The Oxygen Spectrum and Luminous Appearances of Rarefied Gases in Tubes with Liquid Electrodes. By A. Paalzow (*Ann. Phys. Chim.* [2], **7**, 130—136).—In order to eliminate the impurities introduced by metallic electrodes, the author has used an induction tube in which the platinum poles are covered by concentrated sulphuric acid. The luminous appearances obtained are described at length. After considerable passage of the spark, oxygen alone is evolved from the sulphuric acid, the hydrogen at the other pole displacing sulphur from the liquid, and this is precipitated. This enables the author to obtain very constant results for the oxygen spectrum. He finds that it always consists of five bright lines with wave-lengths respectively: $O_\alpha\ \lambda = 602$, $O_\beta\ \lambda = 558{\cdot}2$, $O_\gamma\ \lambda = 519$, $O_\delta\ \lambda = 481$, $O_\epsilon\ \lambda = 453$. The order of brightness is γ, β, δ, ϵ, α. In opposition to Schuster's observations, the spectrum is the same at each pole. He also found this with hydrogen and nitrogen.

As he considers that the use of a Leyden jar vitiates the results, through the detachment of particles from the electrodes and walls of the tube, he only used the simple induction current. His experiments lead him to consider the question still open as to whether a pure gas has several spectra. He inclines to the opinion that it has only one, as he obtained the same five lines for oxygen from a pressure of 200 mm. down to the greatest rarefaction, the best effect being obtained under a pressure of 2 mm. J. H. P.

Spectrum of Ytterbium. By L. de Boisbaudran (*Compt. rend.*, **88**, 1342—1344).—The author has mapped the spectrum of ytterbium obtained by submitting the chloride to the action of the electric spark. The spectrum is formed principally of bands between the lines D and F. For a detailed account of the results reference must be made to the original paper. L. T. O'S.

Spectrum of Didymium Nitrate. By J. L. Smith and L. de Boisbaudran (*Compt. rend.*, **88**, 1167).—Didymium nitrate in neutral or

slightly acid solutions gives an absorption spectrum almost identical with that of the chloride, the lines composing the bands being, however, less distinct. The addition of nitric acid brings about remarkable changes. (1.) The broad band near D fades away almost entirely on the more refrangible side, whilst the less refrangible portion retains its original intensity. If a considerable excess of nitric acid is added, the band retains its original intensity throughout its entire breadth. (2.) The double band near *b* undergoes a similar change even when the acid is added in considerable excess. (3.) The band in the blue 475·8 disappears entirely, and a new band comes out at 473·5—473·0.

C. H. B.

Spectrum of Erbium Nitrate. By L. de Boisbaudran (*Compt. rend.*, **88**, 1167—1168).—Erbium nitrate gives an absorption spectrum identical with that of the chloride. The addition of water weakens the line 540·9, whilst it intensifies the group near *b*, which also increases in breadth. On the other hand the addition of an equal volume of nitric acid weakens the line 683·7 and the group near F, whilst the line 487·4 disappears. The group near *b* and the broad band 451·5 are more intense in the nitric acid than in the aqueous solution.

C. H. B.

Stokes's Law. By S. Lamansky (*Compt. rend.*, **88**, 1192—1196).—Lommel has endeavoured to show that this law is not general, and that in some cases, the fluorescent ray has a greater refrangibility than the exciting ray. Brunner and Lubarsch have confirmed Lommel's experiments, but Hagenbach has not obtained the same result. The author has studied the action of monochromatic light on solutions of fluorescein, eosin, naphthalene-red, and chlorophyll, of varying degrees of concentration and in layers of varying thickness. He finds that *in every case the fluorescent ray is less refrangible than the exciting ray.*

C. H. B.

On a Note by S. Lamansky on "Stokes's Law." By E. Becquerel (*Compt. rend.*, **88**, 1237—1239).—The author confirms the accuracy of Lamansky's experiments, but points out that the phenomenon of fluorescence is not due simply to a change in the refrangibility of the incident light, but is an effect brought about by a change in the vibration of the molecules of the fluorescent body, this vibration being excited by the rays falling upon, and absorbed by, that body. This is replied to by Lamansky in *Compt. rend.*, **88**, 1351—1352.

C. H. B.

Fluorescence of the Salts of the Earth-metals. By J. L. Soret (*Compt. rend.*, **88**, 1077).—The author exposes solutions of chlorides and sulphates of the metals of the rarer earths to the ultra-violet rays of the induction spark taken between poles of cadmium. The solutions are contained in vessels made of quartz, and the rays are concentrated by a lens of the same substance, for glass intercepts the rays which produce the fluorescence. The paper gives a list of the colours observed with salts of cerium, lanthanum, didymium, terbium, erbium, yttrium, ytterbium, philippium, thorium, zirconium, glucinium, and aluminium.

R. R.

Influence of Coloured Light on the Evaporation of Water. By A. Baudrimont (*Compt. rend.*, **89**, 41—43).—Different coloured light exerts a certain influence on the evaporation of water. Green and red light are least favourable to it, whilst yellow and white light are most favourable, and the complementary colours, blue and green, have nearly the same influence.

This is accounted for by the author on the supposition that heat is essentially distinct from light; that it is due to the vibration of the molecules, and not like light to the vibration of the constituent elements, that the vibrations which produce it are of greater amplitude, and less numerous in the same space of time, and are propagated with less velocity. L. T. O'S.

Some Galvanic Properties of Aqueous Solutions of Metallic Salts. By C. Freund (*Ann. Phys. Chem.* [2], **7**, 64—66).—This is stated to be essentially a continuation of G. Wiedemann's research on the motion of fluids in the closed galvanic circuit. It was necessary as a preliminary to find the resistances of the solutions employed, and for this purpose the method already applied by Paalzow (*Pogg. Ann.*, **137**, 489) was used. This was shown to be trustworthy by the agreement of the results with those obtained by Kohlrausch, where they admitted of comparison. Those for $ZnSO_4$, however, gave a conductivity about 5 per cent. greater than that obtained by Beetz, which the author accounts for by supposing that Beetz included in his resistance that of a layer of electrolytically separated gas on the electrode. He considers his own results more correct, since they agree better with those of Kohlrausch and others. The constants in the formula $\kappa_t = \kappa_0 (1 + \alpha t + \beta t^2)$ when κ_t is the conductivity at temperature $t°$, were determined for $ZnSO_4$, $CuSO_4$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$. To measure the difference of pressure caused by the transference of liquid from the positive to the negative pole, the author used a porous cell containing the negative electrode, and filled with the solution to be experimented on. This was connected with a manometer, and immersed in a vessel also containing the solution and the positive electrode.

For $CuSO_4$ the value of $\frac{H\kappa}{J}$ (when H was the increase of pressure in the porous cell, as indicated by the manometer, κ the conductivity, and J the intensity of the current) was found to be constant for the same temperature whatever the concentration, but to rise with the temperature.

For $ZnSO_4$, on the contrary, $\frac{H\kappa}{J}$ was found to depend on the amount of salt in solution. It increased both with the amount in solution and with the temperature. For extremely dilute solutions, it approached a limiting value nearly the same as that for $CuSO_4$. Experiments were also made with a modified form of the apparatus to determine the amount of zinc sulphate solution conveyed through the porous cell.

For $Cu(NO_3)_2$ and $Zn(NO_3)_2$, $\frac{H\kappa}{J}$ diminished as the concentration

increased, and in a constant proportion the same for both. In some experiments on the molecular conductivity of certain double aluminium salts the author found it approximately constant for different salts, and equal to the sum of the molecular conductivities of the constituent simple salts. J. H. P.

Electric Conductivity of Zinc Sulphate Solution. By W. Beetz (*Ann. Phys. Chem.* [2], **7**, 66—70).—This is a reply to the remarks of Freund on the author's method in the above paper. For weak solutions, the author acknowledges that his method is not applicable, but this is clearly stated in the paper quoted by Freund. There he shows under what conditions his method may be used, and proves that then the layer of electrolytically separated gases does not exist. For very concentrated solutions, his results agree with those of Kohlrausch more closely than those obtained by Paalzow's method.

J. H. P.

Capacity of Voltaic Polarisation. By R. Blondlot (*Compt. rend.*, **89**, 148—151).—The author has measured the amount of electricity required to polarise the electrodes of a voltameter, using a current of feeble electromotive force. When the electromotive force is low, there is an approximate relation between the charge and the electromotive force of polarisation; when it is high, the charge increases more rapidly than the polarisation. For a given electrode and electrolyte, the initial capacity does not depend on the kind of polarisation. C. H. B.

Refraction of Invisible Heat. By P. Desains (*Compt. rend.*, **89**, 189—190).—The author has examined the spectra obtained by the action of prisms of flint or crown glass on the rays emitted by incandescent platinum, after their passage through water. He has found in each case a system of three bands situated at the following angular distances from D:—

Crown	45′	56′	65′
Flint	81′	93′	100′

With flint glass another band was observed at 132′ from D, or 90′ from the extreme red, and this same band was found in the solar spectrum. The author concludes that if a section equal in breadth to a third or a quarter of the visible red be isolated from a pure spectrum, although the rays in this section are almost identical as regards refrangibility, they are not so as regards absorption. C. H. B.

Amalgams of the Alkali-metals, and the Nascent State. By Berthelot (*Compt. rend.*, **88**, 1108—1112).—The paper describes the thermic phenomena of the action of water, and of diluted hydrochloric acid on amalgams of potassium and of sodium. The results show that in their hydrogenating reactions, these amalgams disengage more heat than free hydrogen would disengage. This thermic excess, together with the series of reactions induced by the alkalis, explains the great hydrogenating power of the amalgams, a circumstance for-

merly referred to *the nascent state*, the true interpretation of which was first pointed out by the author in 1865 (*Ann. Chim. Phys.* [4], **18**, 61, 66, and 15, and *passim*). R. R.

Thermochemical Studies of the Alkaline Sulphides. By P. Sabatier (*Compt. rend.*, **89**, 43—47).—*Sodium Sulphides.*—1. Anhydrous Na_2S, prepared by heating $Na_2S.9H_2O$ in a current of hydrogen, when dissolved in 120—140 parts of water, evolves 15 cal.

2. $Na_2S.5H_2O$, prepared by dissolving sulphur in warm caustic soda, crystallises in needles. For one equivalent of the sulphide dissolved in 60—120 parts of water at 12° the heat evolved = − 6·6 cal.

3. $Na_2S.9H_2O$, when dissolved in 60—105 parts of water, evolves − 16·72 cal.

From these results may be deduced—

(1.) Heat of formation of anhydrous sodium sulphide—

$$Na_2 + S = Na_2S \text{ disengages} + 88{\cdot}2 \text{ cal.}$$

(2.) Heat of hydration—

Na_2S anhydrous + $5H_2O$ = $Na_2S.5H_2O$ (water solid) + 14·46 cal.
Na_2S „ + $9H_2O$ = $Na_2S.9H_2O$ „ + 18·86 „
$Na_2S.5H_2O$ + $4H_2O$ = $Na_2S.9H_2O$ „ + 4·40 „

Sodium Hydrosulphides.—(1.) $Na_2S.H_2S$ anhydrous, when dissolved in 104—830 parts of water at 10—16°, evolves + 8·8 cal.

(2.) $Na_2S.H_2S.4H_2O$ prepared by carefully evaporating a solution of the hydrosulphide in an atmosphere of sulphuretted hydrogen. On cooling, long clino-rhombic needles separated out, 1 equivalent of which dissolved in 60—100 parts of water at 17·5° evolves − 3·06 cal.

Heat of formation of Hydrosulphide.

Na_2 + S_2 (solid) + H_2 = $Na_2S.H_2S$ (anhydrous) + 110·34 cal.
Na_2S + H_2S = $Na_2S.H_2S$ „ + 18·60 „
2NaHO solid + $2H_2S$ gaseous = $Na_2S.H_2S$ + H_2O gas + 16·30 „

Heat of Hydration.

$Na_2S.H_2S$ anhydrous + $4H_2O$ solid = $Na_2S.H_2S = 4H_2O$ + 6·14 cal.

Potassium Sulphides.—K_2S anhydrous. It is impossible to prepare this substance pure, from the readiness with which it attacks glass. By the dehydration of $K_2S.2H_2O$ a substance containing 20 per cent. of silicate is obtained. From this substance the heat of solution obtained is + 8·2 cal., which gives the heat of formation—

K_2 + S (solid) = K_2S (anhydrous) evolves + 104·2.

$K_2S.2H_2O$, when dissolved in 230 parts of water, evolves + 3·8 cal.

$K_2S.5H_2O$, when dissolved in 75—90 parts of water, evolves − 5·2 cal. From this is deduced—

$K_2S.2H_2O$ + $3H_2O$ solid = $K_2S.5H_2O$ disengages + 4·6 cal.

Potassium Hydrosulphides.—$K_2S.H_2S$ prepared by the dehydration

of $K_2S.H_2S.H_2O$ in a current of H_2S. 1 equivalent dissolved in 45—240 parts of water at 16° evolve + 1·34 cal.

From this it is found—

Heat of Formation of Potassium Hydrosulphide.

$K_2 + S_2$ (solid) + $H_2 = K_2S.H_2S$ (anhydrous) disengages + 128 cal.

K_2S (anhydrous) + H_2S. gaseous = $K_2S.H_2S$ (anhydrous) disengages + 19·0? ,,

$2KHO$ solid + $2H_2S$ gaseous = $K_2S.H_2S$ (anhydrous) + H_2S gaseous, disengages + 28·96 ,,

Heat of Hydration.

$K_2S.H_2S$ (anhydrous) + H_2O = $K_2S.H_2S.H_2O$ (solid water) − 1·22 cal.

,, ,, ,, ,, (liquid water) + 0·20 ,,

The last result forms an example of a saline hydrate produced with absorption of heat when formed from solid water. L. T. O'S.

Thermochemical Study of Dissolved Alkaline Sulphides. By P. Sabatier (*Compt. rend.*, **89**, 234—236).—Although alkaline monosulphides cannot exist in dilute solutions, the addition of a concentrated solution of an alkali to a concentrated solution of a sulphhydrate is attended with an evolution of heat, indicating the formation of a small quantity of monosulphide. The amount of heat thus evolved decreases with the dilution of the solutions, and at last becomes nil. The influence of dilution on the formation of alkaline sulphides from the alkali and gaseous hydrogen sulphide has also been studied. The heat of formation of potassium sulphhydrate decreases slowly with increased dilution; that of sodium sulphhydrate remains nearly constant. C. H. B.

Etherification. By Berthelot (*Bull. Soc. Chim.* [2], **31**, 341—354).—With a view to arrive at the theory of the reaction caused by mineral acids in the formation of compound ethers, the author has conducted the following chemical and thermal experiments:—

I. *Chemical Experiments.*—Hydrochloric acid was absorbed by a mixture of equivalent parts of alcohol and acetic acid, so as to form mixtures of the following constitution:—

	grams.	grams.
(1.) $C_2H_4O_2 + C_2H_6O + \frac{1}{60}$ HCl, or for	106 mixture..	0·67 HCl.
(2.) $C_2H_4O_2 + C_2H_6O + \frac{1}{8}$ HCl ,,	,, ..	4·77 ,,
(3.) $C_2H_4O_2 + C_2H_6O + \frac{1}{3}$ HCl ,,	,, ..	11·84 ,,

In each mixture the quantity of free hydrochloric acid and the sum of the two acidities were estimated, with the following results:—

Conditions of Experiment.	Mixture 1. Proportion of Acid converted into Ether.			Mixture 2. Proportion of Acid converted into Ether.		
	Total.	Acetic Acid.	HCl.	Total.	$C_2H_4O_2$.	HCl.
In the Cold.						
Soon after absorption ...	9·6	9·6	0·0	58·7	58·7	0·0
Six hours after ,, ..	—	—	—	73·6	73·6	0·0
Eight days after ,, ..	68·3	68·3	0·0	73·8	73·8	0·0
One month after ,, ..	67·5	68·5	0·0	—	—	—
At 100°, 10 hours after absorption	67·7	67·7	trace	75·0	68·8	47·0
At 100°, 50 hours after absorption	67·4	66·2	60·0	75·1	66·4	67·0
At 200°, 12 hours after absorption	65·3	63·7	89·0	58·3	47·0	87·0

Conditions of Experiments.	Mixture 3. Proportion of Acid converted into Ether.		
	Total.	$C_2H_4O_2$.	HCl.
In the Cold.			
Soon after absorption ...	72·3	72·3	0·0
Six hours after ,, ..	75·8	75·8	0·0
Eight days after ,, ..	76·4	76·4	trace
One month after ,, ..	76·4	76·1	1·0
At 100°, 10 hours after absorption	85·3	62·0	72·0
At 100°, 50 hours after absorption	83·7	56·2	84·5
At 200°, 12 hours after absorption	59·5	42·0	95·0

From this the author infers that the addition of the mineral acids leads in a few hours to results which it would take years to obtain without its aid. The acceleration is greater, the more hydrochloric acid there is present; it acts especially by the formation of hydrates, thus removing water from the ether-forming bodies, and the quantity of water removed is greater, the greater the quantity of hydrochloric acid present.

In the cold, with a trace of hydrochloric acid, the limit to the reaction is 68·3, which is practically the same as that with acetic acid alone (66—67). The hydrochloric acid does not combine with the alcohol so long as the quantity of water set at liberty is sufficient to destroy

the tension of the anhydrous acid, this is the case with the mixtures 1 and 2, but in the case of mixture 3, the hydrochloric acid is in excess, and therefore exists partly in the anhydrous state, and consequently forms ethyl chloride; its formation, however, is slower than that of acetic ether. The limit of the etherification is proportional to the amount of acid present.

At 100°, the action is different, the hydrates becoming dissociated. With a trace of hydrochloric acid, the limit remains the same as in the cold; it does not change with time, although a portion of the acetic ether is converted into ethyl chloride; this is possible, since the acid does not exist as hydrate. With mixture 2, no very marked difference is observed, although the acid plays a more active part, 7 per cent. of acetic ether being converted into ethyl chloride. In mixture 3, the limit increases considerably, and ethyl chloride is formed, first at the expense of the alcohol, and then of the acetic ether.

At 200°, the limit is smaller in all the mixtures, notably in mixture 3, it being 24 per cent. less. This is explained by the formation of ether.

By adding water to a mixture of acetic acid and alcohol, in the proportion $C_2H_4O_2 + C_2H_6O + H_2O$, the limit of the reaction is 59·4; this is not materially increased by the presence of traces of mineral acid. In the case of 1·9 grams HCl the limit in the cold and at 100° was 60·6; and of 2 grams H_2SO_4, it was 59·6 in the cold, and at 100° 66·6.

In the cold, the alcohol combines with the acetic acid so long as the quantity of hydrochloric acid is only sufficient to form definite hydrates with the water produced by the reaction, and thus destroy the tension of the acid; but if the quantity of hydrochloric acid is more than sufficient to form a hydrate, then ethyl chloride is slowly formed at the expense of the acetic ether. At 100°, the same reaction takes place slowly, both by the direct union of hydrochloric acid and alcohol, and the decomposition of the acetic ether. This is the case with all the mixtures, the hydrate formed being dissociated.

At 200°, ethyl chloride is formed at the expense of the alcohol, acetic ether, and ether, the last body being formed by a secondary reaction.

To prove that ethyl chloride is formed at the expense of the acetic ether, acetic ether was treated with hydrochloric acid in the cold, and at the end of 17 days a trace of ethyl chloride was formed; in five weeks the quantity had increased. When heated in sealed tubes to 100°, the reaction takes place at once, and at 200°, ethyl chloride is formed, according to the equation $C_2H_5(C_2H_3O_2) + HCl = C_2H_5Cl + C_2H_4O_2$.

II. *Thermal Experiments.*—The influence of the heat of formation of the compounds produced in the reciprocal reaction of the different bodies on the formation of the ethers may be seen from the following. The crystallised hydrate $HCl + H_2O$ is formed in the liquid state with the disengagement of + 11·6 cal., and even in the cold the acid possesses considerable tension; the liquid hydrate $HCl + 6·5\ H_2O$, of which the heat of formation is 14·0 cal., loses all tension at the ordinary temperature. With excess of water at 18°, the heat of formation

is 17·4 cal. Alcohol absorbs hydrochloric acid, forming bodies resembling the crystallised compounds of dulcite with hydrochloric acid. The acid is only held in solution, and on distillation is evolved, but at 83° a liquid $HCl + 3{\cdot}2C_2H_6O$ distils over. By the evaporation at 12° of the mixtures $HCl + 1{\cdot}2C_2H_6O$, and $HCl + 4{\cdot}5C_2H_6O$, others are obtained of the constitution $HCl + 3{\cdot}1C_2H_6O$ in the first case, and $HCl + 3{\cdot}3C_2H_6O$ in the second; it is therefore evident that a body, $HCl + 3C_2H_6O$, exists analogous in composition to $HI + 3H_2O$.

The heat disengaged by the action of hydrochloric acid on alcohol is—

$HCl + 1{\cdot}15C_2HO$	at 12°		+ 10·8 cal.
$HCl + 1{\cdot}59$	,,		+ 11·5 ,,
$HCl + 300$	,,		+ 17·35 ,,

from which is obtained $HCl + C_2H_6O = + 10{\cdot}6$ and $HCl + 3C_2H_6O = + 13{\cdot}8$, numbers nearly corresponding with those of the hydrates.

Hydrochloric and acetic acid at 13° forms the compound $HCl + 5{\cdot}8C_2H_4O_2$, which loses all the HCl by distillation, but by evaporation in a current of air, the following compounds are obtained :—

HCl gas +	$5{\cdot}8C_2H_4O_2$	at 13°	disengages	..	+ 6·22 cal.
HCl ,, +	41·0	,,	,,	..	+ 7·10 ,,
HCl ,, +	200	,, 16°	,,	..	+ 7·09 ,,

values less than half of those obtained for water and alcohol, showing that these compounds cannot be formed in their presence. The formation of acetic chloride from acetic acid and hydrochloric acid requires the absorption of −12·6 cal., therefore it cannot be formed by the direct union of the two acids, but requires some external agent to supply the heat necessary to bring about the inverse of the reaction $C_2H_3OCl + H_2O = C_2H_4O_2 + HCl$ gas $= + 5{\cdot}5$.

Hydrochloric acid forms three different compounds with acetic ether. Saturated at 12° it forms $HCl + 1{\cdot}36C_2H_5.C_2H_3O_2$. $HCl + 6{\cdot}1C_2H_5.C_2H_3O_2$ is obtained by evaporation of the former compound in a current of air for two hours, and after six hours the compound $HCl + 12C_2H_5.C_2H_3O_2$ is formed. The quantities of heat disengaged are intermediate between the compounds of acetic acid and those of the alcohol and water compound, thus :—

$HCl + 1{\cdot}36C_2H_5.C_2H_3O_2$	saturated	at 12°	disengages	..	+ 8·82 cal.
$HCl + 2{\cdot}64$	,,	,,	,,	..	+ 9·82 ,,
$HCl + 11{\cdot}84$	,,	,,	,,	..	+ 11·84 ,,

At 200°, these compounds are rapidly changed into ethyl chloride and acetic acid, but more slowly at 100° and in the cold. This reaction, therefore, cannot be regarded as the one which accelerates the formation of acetic ether in presence of hydrochloric acid.

Ethyl chloride does not dissolve appreciable quantities of hydrochloric acid.

The compounds formed by acetic acid with water and alcohol are very unstable, as seen by the small quantity of heat disengaged.

$C_2H_4O_2 + H_2O$		− 0·15
$C_2H_4O_2$ + excess of water	at 7°....	+ 0·40
$C_2H_4O_2 + C_2H_6O$	at 12°....	− 0·06
$2C_2H_4O_2 + C_2H_5(C_2H_7O_2)$	at 13°....	+ 0·26
$1·27C_2H_4O_2 + C_2H_5Cl$	at 13°....	+ 0·20

Alcohol and the ethers when dissolved in a large proportion of water evolve small quantities of heat.

C_2H_6O at 12° + 2·6 cal.; $C_2H_5(C_2H_3O_2)$ at 16° + 3·1.

The heats disengaged by the union of the various other compounds are—

$C_2H_6O + 0·59C_2H_5(C_2H_3O_2)$	at 12° ..	about	− 0·09
$1·7C_2H_6O + C_2H_5(C_2H_3O_2)$	,, ..		− 0·15
$1·23C_2H_6O + C_2H_5Cl$	,, ..	,,	− 0·2
$C_2H_5Cl + 0·93C_2H_5(C_2H_3O_2)$	,, ..	,,	− 0·08

By comparing these results, it is seen that the heat disengaged in the formation of acetic ether is in excess of that of ethyl chloride, thus:—

Ethyl Acetate.

C_2H_6O liq. + $C_2H_4O_2$ liq. = $C_2H_5(C_2H_3O_2)$ liq. + H_2O liq. absorbs	− 2·0	
Solution of $C_2H_5(C_2H_3O_2)$ in excess of alcohol absorbs	− 0·1	+ 15·6
Solution of water in excess of alcohol absorbs.....	+ 0·3	
Solution of HCl gas in excess of alcohol absorbs ..	+17·4	

Ethyl Chloride.

C_2H_6O liq. + HCl gas = C_2H_5Cl liq. H_2O liq. disengages	+ 6·0	
Solution of C_2H_5Cl in excess of alcohol disengages..	− 0·3	+ 5·9
Solution of water in excess of alcohol disengages ..	+ 0·3	
Solution of $C_2H_4O_2$ in excess of alcohol disengages..	− 0·1	

It is therefore evident that the formation of ethyl acetate is the first reaction to take place. In presence of excess of water, the heat of formation of ethyl acetate is 18·5°, and that of ethyl chloride, 5·8°. In this case also, the first reaction is the one to take place. It is for a similar reason that benzoic chloride when treated with alcohol forms ethyl benzoate rather than ethyl chloride.

The acceleration in the etherification caused by the hydrochloric acid is therefore due to the great amount of heat generated in the formation of hydrates and analogous bodies by the mineral acid. This applies to all acids, for by distilling a mixture of alcohol and acetic acid, containing a few drops of nitric acid, ethyl acetate is formed in considerable quantities. The same explanation shows why benzene, when treated with a mixture of nitric and sulphuric acid, yields a nitro and not a sulphonic derivative, for $C_6H_6 + H_2SO_4 = C_6H_5.HSO_3 + H_2O = + 14·4 - \alpha$, and $C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O = + 36·6$. α = heat of solution of benzenesulphonic acid in water.

It is therefore the excess of energy displayed by the mineral acids

compared with the organic acid which causes the former to give place to the direct actions of which the latter, by themselves, are capable of only in a slight degree. L. T. O'S.

Thermic Effect of Substitutions. By W. Louguinine (*Ann. Chim. Phys.*, [5], **16**, 229—268).—The substances used in these experiments were :—1. Aniline, toluidine, and their derivatives. 2. Acetic and benzoic acids and their derivatives. 3. Substitution compounds of phenol. The method of operating and the apparatus employed were similar to those which have already been described by Berthelot.

Aniline.—1 molecule of aniline in grams was dissolved in 4 litres of water, and 1 molecule of HCl in 2 litres. The heat evolved by the union of the acid and base was 7·442 thermal units; this number became 7·342 when the base was not previously dissolved, consequently −0·1 represents the heat absorbed in the solution of the aniline. By decomposing aniline hydrochloride with caustic soda, the experimental number was 6·316 units; correcting this, and deducting it from Berthelot's equivalent for the union of chlorine and sodium, we get (13·69−6·416) = 7·274 units. In a similar manner, by decomposing the hydrochloride by ammonia, the number of units obtained was 7·391.

The author gives the preference to the number resulting from the first direct experiment, since the solution of aniline hydrochloride in water is attended with a notable absorption of heat; this absorption is, however, less than that found by Berthelot and Thompson for the solution in water of ammonium chloride.

The heat of neutralisation of aniline by nitric acid was 7·448 units when directly determined. By decomposing the nitrate with soda as in the previous instance, 6·994 units were obtained; this lower result is likewise probably due to incipient decomposition of the aniline nitrate after solution.

By substituting oxalic acid for nitric acid, 7·66 thermal units were observed; the three acids, therefore, hydrochloric, nitric, and oxalic, acting upon aniline in equal equivalents (1 to 1), disengaged very nearly the same amount of heat, whilst the numbers obtained are evidence that aniline is a base very much weaker than its analogue ammonia.

Paratoluidine.—3·617 grams of a slightly coloured, and 3·419 grams of a white specimen were dissolved respectively in 1 litre of water, and the heat of neutralisation by hydrochloric acid determined. The coloured sample gave slightly higher results than the white one, the mean being 8·238 thermal units, everything remaining dissolved. The action of HCl on the undissolved base evolved 4·528 units, which gives −3·71 units for the heat absorbed in the solution of 1 molecule in grams of the base. The calorimetric effect of the action of aniline on toluidine hydrochloride was so small as to be scarcely measurable, −0·066 unit; from which it is reasonable to conclude that toluidine is not entirely displaced from its combination with hydrochloric acid by aniline. This hydrochloride, moreover, is very stable in solution in water, requiring large dilution to effect even a slight decomposition.

Orthochloraniline.—6·274 units represents the heat evolved in the neutralisation of the dissolved base by hydrochloric acid, and 5·713 units, the heat of neutralisation of the undissolved base, consequently the heat absorbed during the solution of the base in water is 0·561 unit. By fractionally precipitating the hydrochloride by the addition of soda in three successive portions, and taking the heat evolved after the last addition of alkali to represent exactly one-third of the total heat generated, 5·464 units were obtained. Further, by substituting aniline for soda, the number became 5·038, showing that orthochloraniline was capable of being wholly displaced by aniline.

Meta- and *Para-chloraniline.*—Operating in the same manner, the thermal units obtained were—

	Meta.	Para.
By direct addition of HCl	5·778	7·198
By decomposition of salt with soda solution..	5·654	1·193?
By fractional decomposition with soda.....	5·797	—
By decomposition with aniline	5·693	2·319

In the case of the para-derivative, the difference between the number found by decomposition with soda, and that obtained directly, is probably due to an error in the determination of the heat absorbed in the solution of the base; and the low number obtained by the use of aniline shows that parachloraniline is not entirely displaced by the non-substituted base; this latter fact might have been foreseen, since the heat of combination of the dissolved para-base approaches that of aniline itself, and is sensibly higher than that of its two isomerides.

Paranitraniline evolves 1·811 units of heat when, having been previously dissolved, it is brought into combination with HCl, but it absorbs −1·926 units when treated with HCl without previous solution; this is due to the fact that the solution of paranitroaniline in water absorbs a greater amount of heat (−3·737 units) than that evolved during its combination with hydrochloric acid. The conclusions drawn from the foregoing experiments are:—1. That the heat disengaged in the combination of the substituted bases of the aniline group is sensibly diminished when an atom of H is replaced by Cl or NO_2; that the introduction of the group NO_2 produces a greater reduction in the heat evolved during combination with HCl than the introduction of an atom of Cl. 2. That the isomeric monochloranilines do not disengage the same quantities of heat under similar circumstances, the ortho- and meta-derivatives evolving less than the para-derivative.

Acetic Derivatives.

	Monochloracetic acid.	Trichloracetic acid.
1. Neutralisation with soda	14·354	14·056
2. Solution of the acid in water	−2·331	+2·894
3. Undissolved acid acting on soda solution	11·972	17·055
4. Indirect determination from 2 and 3 ..	14·302	14·161

	Amido-acetic acid.	Amido-propionic acid.
1. Neutralisation with soda	2·967	2·467
2. Direct combination with HCl.....	0·980	0·896
3. Decomposition by soda of combination with HCl.....	12·852	—
4. Solution of the acid in water	−3·580	—

The replacement of H by Cl in acetic acid slightly augments the amount of heat disengaged during the combination of the acid with alkali, but there is no regularity in the increase, for it appears that monochloracetic acid evolves more heat in this reaction than does trichloracetic acid.

The introduction of NH_2 for H alters altogether the character of the compound, the acid becomes almost a neutral body, capable of combining very feebly both with acids and bases. These amido-acids, however, disengage more heat in uniting with soda than in combining with hydrochloric acid.

Benzoic Derivatives.—The following table shows the number of thermal units obtained for nitro- and amido-benzoic acids in comparison with ordinary benzoic acid.

	Benzoic.	Nitro-benzoic.	Amido-benzoic.
Acid dissolved, base and salt dissolved ..	13·500	12·80	9·27
,, solid ,, ,, ..	7·000	7·71	5·11
,, dissolved ,, salt solid ..	12·700	14·07	7·87
,, solid ,, salt solid ..	6·200	8·98	3·72
All separated from the water, and with the water, referred to the solid condition	17·4	20·1	14·9

Whilst the substitution of H by NO_2 in benzoic acid influences materially the heat of combination with soda when all the reacting bodies are referred to the undissolved condition, the effect is much less obvious when everything is dissolved. In this respect it resembles the substitution by Cl. The group NH_2, on the other hand, diminishes considerably the heat disengaged under all conditions, but it obviously does not affect the character of the molecule so powerfully as it does in the fatty series. If the energy of the amido-acids of the acetic series be compared with that of hydrocyanic acid, the corresponding acids of the benzoic series might be compared with carbonic or boric acids.

Phenol Derivatives.

	Ortho.	Meta.	Para.	Dichlor.
Substance dissolved, base dissolved, combination dissolved	9·33	7·82	8·92	9·06
Substance solid, base dissolved, combination dissolved	2·97	7·16	4·09	4·77
Substance dissolved, base dissolved, combination solid	12·61	—	—	—
Substance solid, base dissolved, combination solid	6·28	—	—	—
All separated from the water, and with the water, referred to the solid condition.....	17·4	—	—	—

Taking the difference between the heats of neutralisation of phenol (7·4 units) and of picric acid (13·8 units), and dividing this by 3, we get the number 2·13, corresponding to the introduction of NO_2 into the phenol. If we add this number to 7·4, the calculated number for mononitrophenol would become 9·53, which is not very far removed from the experimental numbers for ortho- and para-nitrophenol. It is probable that the heat of combination of the substitution-products of phenol increases proportionately with the number of times that the residue NO_2 is introduced; if such be the case, the heat of combination of dinitrophenol should be about 11·66 units, according to the particular isomeride operated on. The introduction of the grouping NO_2 has a greater effect upon the phenol molecule than the introduction of a corresponding amount of Cl; as far as the heat of neutralisation may be taken as evidence, the single group NO_2 is about equivalent to Cl_2.

J. W.

Some Thermochemical Data. By Berthelot (*Compt. rend.*, **89**, 119—121).—(1.) *Formation of Gaseous Diamylene.*—The specific heat of diamylene, $C_{10}H_{20}$, between 20° and 130° is 0·545; its molecular heat, 76·3; heat of vaporisation, $C_{10}H_{20}$, 140 grams = 6·91. The heat disengaged by the conversion of liquid amylene into liquid diamylene is 11·8 cal. The heat of vaporisation of amylene is 5·25: hence the conversion of gaseous amylene into gaseous diamylene, $2C_5H_{10} = C_{10}H_{20}$, disengages 15·4 cal.

(2.) *Heat of Fusion, and Specific Heat of Glycerol.*—The heat of fusion of glycerol, $C_3H_5(OH)_3$, 92 grams = 3·91 cal. Determinations of the specific heat gave the following numbers:—

	Sp. heat.	Mol. heat.
Between 14 and 100°.....	0·591	54·4
„ 16 „ 179	0·646	59·4
„ 20 „ 195	0·665	61·1

or $47·8 + 0·14\,t$ at temperature t.

The specific heat of dilute solutions of glycerol is sensibly greater than that of water, and therefore greater than the mean of the specific heats of their constituents.

C. H. B.

Observations on Noble and Abel's Memoir "On the Combustion of Gunpowder." By BERTHELOT (*Compt. rend.*, **89**, 192—196).—The author points out that the new calorimetric results obtained by Noble and Abel more nearly approach the theoretical numbers, but considers that it is not sufficient simply to read the highest temperature attained by the water in the calorimeter, since the explosion vessel still gives up heat to the water during the first minutes of the period of cooling. Comparative observations should be made as to the rate of cooling of the calorimeter when filled with water at the maximum temperature attained, other conditions remaining the same. The thiosulphate found in the solid residue is probably a secondary product formed by the action of sulphur dioxide, or nitrous vapours, on the sulphide present, when the apparatus has cooled. It cannot be a direct product of the explosion, the temperature of which is 2200°, since it is decomposed at 550°.

The combustion of an explosive compound, *e.g.*, gun-cotton, gives rise to simpler products than the combustion of an explosive mixture, *e.g.*, gunpowder, because of the molecular homogeneity of the former. C. H. B.

Vapour-densities of some Inorganic Compounds. By V. and C. MEYER (*Deut. Chem. Ges. Ber.*, **12**, 1282—1285).—The authors have determined the vapour-density of antimony trioxide at 1500° C., using their method already described (*Ber.*, **12**, 1112). The numbers obtained show the molecular weight to be Sb_4O_6, similar to that of arsenic trioxide. Cuprous chloride at the same temperature gives 6·93 as the density, Cu_2Cl_2 requiring 6·84. Cadmium bromide gave the following numbers: vapour-density at 923° = 9·22, at 914° = 9·28, whereas 9·84 is the calculated number for $CdBr_2$. The authors hope to determine the vapour-density of glucinum chloride. P. P. B.

Study of the Molecular Constitution of Liquids by Means of their Coefficient of Dilatation, Specific Heat, and Atomic Weight. By R. PICTET (*Compt. rend.*, **88**, 1315—1319).—In a previous note (*ibid.*, **88**, 855) the author has shown that there exists a simple relation between the atomic weights of solid bodies, their temperature of fusion, and length of calorific oscillation. In the present paper he has extended his researches to liquids, and concludes that, if temperature be regarded as length of calorific oscillation, a simple relation exists between the atomic weights, dilatations, and temperatures of changes of state of *all* bodies. C. H. B.

Exsiccator for Carbon Bisulphide, Ether, Chloroform, and Benzene (*Deut. Chem. Ges. Ber.*, **12**, 1294).—In order to evaporate an ethereal solution, without the application of heat, the liquid is placed in an ordinary desiccator in which sulphuric acid is replaced by crude paraffin. The ether is absorbed by the paraffin, and may be recovered by distilling the mixture. The apparatus may also be employed for the evaporation of liquids containing chloroform, carbon bisulphide, and benzene. W. C. W.

Distillation of a Heterogeneous Liquid. By L. TROOST (*Compt. rend.*, **89**, 229—231).—Engel and Moitessier (*Compt. rend.*, **88**, 285)

have stated that when a mixture of chloral hydrate and chloroform is distilled, the vapour which passes over at about 61° contains chloroform, water, and anhydrous chloral. The author has found that when 20 grams of chloral hydrate are distilled with 200 grams of chloroform, water-vapour and chloroform pass over at 61°, and anhydrous chloral remains in the retort, together with a portion of the chloroform. Almost the whole of the water contained in the chloral hydrate has passed over when two-thirds of the mixed liquid has been distilled. Since the tension of water-vapour is 50·2 mm. less than that of anhydrous chloral, it is probable that the latter is retained in the retort in consequence of chemical action. C. H. B.

Viscosity a cause of Catalysis. By A. Guyard (*Bull. Soc. Chim.* [2], **31**, 354—358).—The reaction of certain metallic salts with known reagents is to some extent modified by the presence of glycerol. Thus, under these circumstances, chromium sesquioxide is not precipitated by ammonia and ammonium chloride, nor yet copper by potash or soda. On the other hand, in presence of glycerol, uranium and bismuth are precipitated by ammonia, and barium and manganese by potash. By adding potash or soda to salts of nickel and cobalt in presence of excess of glycerol, the oxides are partially precipitated on destroying the viscosity, either by adding water or warming the solution; the portion of oxide which always remains in solution colours it from a dirty grey to a magnificent blue.

If glycerol in large excess be mixed with solutions of potassium-titanium sulphate, aluminium sulphate, ferric chloride, lead nitrate, or stannous chloride, and ammonia added, the oxides are not precipitated, but on adding a large quantity of hydrochloric acid, and resaturating the solution with ammonia, the oxides are precipitated; a similar phenomenon takes place when potash or soda is added to solutions of ferric oxide and uranium oxide, or ferrous cobalt and nickel oxide in presence of glycerol. The oxides are precipitated only after saturating the alkaline solution with hydrochloric or sulphuric acid, and then adding a further excess of alkali. These phenomena are due to the viscosity of the glycerol which prevents the precipitation; it is, however, modified by the presence of the alkaline salts formed by the action of the acids on the alkalis.

Titanic acid is not precipitated in presence of glycerol even by excess of ammonia; if, however, a few drops of sulphuric acid be added to the ammoniacal solution without destroying its alkaline reaction, titanic acid is precipitated at once. Alumina is precipitated by ammonia in presence of glycerol as a flocculent instead of a gelatinous precipitate.

These phenomena cannot well be made use of in the separation of the metals; they are however of theoretical interest, as they show how the physical property has been mistaken for a chemical property.

L. T. O'S.

Researches in Chemical Equivalence. By E. J. Mills and J. J. Smith (*Chem. News*, **40**, 15—17).—*Nickel and Cobalt Sulphates.*—Since the combining proportions of nickel and cobalt appear to be quite the same, the authors made it their object to inquire the

terms on which these metals proved to be mutually equivalent. The particular equivalence examined was equivalent precipitability of the sulphates, by sodium hydrate, from an aqueous solution. The sulphates of the two metals having been obtained in a pure form, a 1 per cent. solution of each salt was prepared, and a solution of sodium hydrate, of which 10 c.c. were capable of precipitating 0·8248 gram of nickel and cobalt sulphates. A series of nine experiments was made, in which the relative weights of nickel or cobalt sulphate present varied from 0·1 to 0·9 gram, the total weight of nickel and cobalt salt and the volume of the solution being, however, always the same, viz., 1 gram and 10 c.c. The experiments were conducted as follows:—The bottles containing the solutions of the sulphates and the sodium hydrate were immersed in a trough through which there was a flow of water to bring them to a constant temperature. The necessary quantities of nickel and cobalt solutions were then carefully measured out, mixed, and the temperature observed. 10 c.c. of sodium hydrate were then added, the solution was stirred vigorously, the temperature again observed, the precipitate filtered off, and washed first with cold then with hot water. After washing, the precipitate was converted into sulphate by treatment with sulphuric acid and weighed. The mixed sulphates were then dissolved in water and separated by Gibbs's method, the nickel sulphate being weighed and the cobalt estimated by difference.

In discussing the results of these experiments, which are arranged in a table, the authors find that the precipitability of nickel sulphate is directly proportional to its mass. In the case of cobalt sulphate, on the other hand, no such law holds good. It is also shown that the two sulphates are equally precipitable when the weight taken of each is 0·84093 gram. A highly important chemical relation is disclosed when the two sulphates are conditioned in this manner. The reciprocal of 0·84093 is 1·1892, a number differing by only the small amount of 0·40 per cent. from 1·1845—the mean value of the precipitability of cobalt sulphate. Deduced as these values are from a series of experiments, the authors consider that their connection must be something more than accidental. The relation may be stated thus:—For an equal weight, nickel and cobalt sulphates are equally precipitable, the attraction of the one towards the reagent being then inverse to that of the other. In order to ascertain whether this function admits of extension to other weights than 0·84093 gram of the sulphates, all the masses in one of the previous experiments were doubled, and it was found that the chemical effect produced was also doubled. The authors think it probable that this law is general, and therefore infer that the reciprocal function noticed may apply to multiples of the weights to which, in their particular case, it specially appertained. Bearing in mind that $NiSO_4 = CoSO_4 = 154·65$, they accordingly write the function thus: $\phi(NSO_4) = \phi^{-1}(CoSO_4)$. D. B.

A Simple Gas-holder. By G. Attenkofer (*J. pr. Chem.* [2], **19**, 335).—An ordinary gas-holder with two tubes furnished with stopcocks passing through the top and no other orifice. One of the tubes passes to the bottom of the vessel, the other merely makes a communi-

cation between the vessel and the outer air. Water is run in by the longer tube. When the vessel is full gas is passed in by the shorter tube, while a caoutchouc tube is connected with the longer, so that the water is syphoned out thereby. By again running water in through the longer tube, a stream of gas is forced out through the shorter.

M. M. P. M.

Inorganic Chemistry.

Preparation of Distilled Water free from Ammonia. By J. S. Thomson (*Chem. News*, **40**, 18).—The following modification of the distilling apparatus commonly found in laboratories at once provides a simple means of securing a practically unlimited supply of water free from ammonia, and at the same time requires little or no attention. The tube which conducts the vapour from the still or boiler, in place of being connected directly with the worm, is made to enter at the bottom of a large iron drum, while the top of the drum is connected with the worm-pipe in the ordinary manner. The drum, which is freely exposed to the air, condenses a portion of the aqueous vapour. and the condensed water falling to the bottom, is kept in a state of ebullition by the free steam blowing into it. Now, if this condensed water be drawn off by a suitable tap, it will be found to be perfectly free from ammonia, while the ordinary distilled water at the worm end contains abundance of ammonia. D. B.

Electrolysis of Hydrogen Peroxide. By E. Schöne (*Liebig's Annalen*, **197**, 137—168).—This paper, the author's sixth communication relating to his researches on hydrogen peroxide, describes the results obtained by submitting solutions of that substance to electrolysis. Different statements of the effect of electrolysis on aqueous solutions of hydrogen peroxide have been put forth by different chemists, and the author shows that the reactions may possibly occur in various ways, among which he enumerates the following:—

	Direct electrolysis of the	Secondary actions.	
		At − pole.	At + pole.
1.	Water only— $H_2O = H_2 + O$	$H_2 + H_2O_2 = 2H_2O$	$O + H_2O_2 = H_2O + O$
2.	Peroxide only— $H_2O_2 = H_2 + O_2$	None	None
3.	Do. do.	$H_2 + H_2O_2 = 2H_2O$	None
4.	Do. do.	Do.	$O_2 + 2H_2O_2 = 2H_2O + 2O_2$
5.	Do. $H_2O_2 = H_2O + O$	None	None
6.	Do. do.	None	$O + H_2O_2 = H_2O + O_2$

The table shows that the proportions of the gases collected at each pole, compared with the gases which would be collected in a voltameter included in the same circuit, and with the quantities of undecomposed hydrogen peroxide contained in the liquid round each electrode, would, taken collectively, differ in each case. The author's experiments were directed to the accurate measurement of the quantities concerned. He found that the results were influenced by the strength of the solution, the quantity of acid used to acidulate it, and the strength of the current. But under conditions as to these particulars comprised within tolerably wide limits, he obtained results agreeing throughout with Case 1 of the preceding table. Hence his conclusion, that hydrogen peroxide is not an electrolyte, and that in its (acidulated) solution, it is the water alone (or rather the acid) which is electrolysed, the decomposition of the peroxide being a secondary action, effected by the hydrogen and oxygen in the nascent state as they are liberated from the water. R. R.

Dissociation of Ammonium Sulphide. By R. Engel and Moitessier (*Compt. rend.*, **88**, 1201—1203).—Bineau (*Ann. Chim. Phys.*, **70**, 76) stated that ammonium sulphide exists only at very low temperatures. In 1869, Deville and Troost gave the density of this compound as 1·26 (air = 1). Horstmann, in 1863, concluded, from the results of the determinations of the density of mixtures of hydrogen sulphide and ammonia, that these two gases do not combine at temperatures between 56·4° and 85·9°. The authors find (1) that 2 vols. of ammonia and 1 vol. of hydrogen sulphide combine at ordinary temperatures to form ammonium sulphydrate, 1 vol. of ammonia remaining uncombined; (2) the product dissociates very rapidly with elevation of temperature, and at 45° the dissociation is complete. The gases recombine on cooling. C. H. B.

Dissociation of Ammonium Hydrosulphide. By R. Engel and A. Moitessier (*Compt. rend.*, **88**, 1353—1354).—A bell-jar was filled, over mercury, with equal volumes of ammonia gas and sulphuretted hydrogen and maintained at 50°. On the introduction of a piece of charcoal previously ignited, absorption of the mixed gases took place, and the volume of the gases diminished by three-fourths. The charcoal was then withdrawn, placed in a vacuous bell-jar over mercury, and warmed, when the absorbed gases were expelled. On cooling, crystals formed on the side of the jar, and on introducing a piece of pumice-stone saturated with sulphuric acid, the residual gas was entirely absorbed, showing it to be ammonia. In the case of the gas remaining in the original jar, after the withdrawal of the charcoal, no absorption occurred, showing the absence of ammonia gas.

If combination had taken place on mixing the gases at 50°, condensation would have taken place, but no such effect was noticed, and, moreover, the gases would have been absorbed by the charcoal in equal volumes, and when again expelled by heat would not have contained excess of ammonia. The formation of crystals on the sides of the jars shows that combination takes place on cooling.

It is therefore evident that at 50° ammonium hydrosulphide does not exist, but is dissociated. On cooling, however, the gases reunite, forming the original compound. L. T. O'S.

Dissociation of Ammonium Hydrosulphide. By Isambert (*Compt. rend.*, **89**, 96—97).—In reply to the above, the author claims priority (*Ann. de l'École Normal Supérieure*, **5**, 153), and states that the results of Engel and Moitessier only show that charcoal absorbs ammonia gas more readily than ammonium hydrosulphide. L. T. O'S.

Dissociation of Ammonium Hydrosulphide. By R. Engel and A. Moitessier (*Compt. rend.*, **89**, 237).—This is a reply to the objections raised by Isambert (*Compt. rend.*, **89**, 96) against the author's proofs of the dissociation of ammonia hydrosulphide at moderate temperatures. They find, in addition to the proofs already given (*Compt. rend.*, **88**, 1353), that when a few drops of water are introduced into a mixture of equal volumes of hydrogen sulphide and ammonia at a low temperature, the gas is absorbed as a whole; if, however, the gaseous mixture and the water be previously heated to 50°, the ammonia alone is dissolved. C. H. B.

Basic Hydrosulphides of Ammonia. By L. Troost (*Compt. rend.*, **88**, 1267).—Several of these compounds have been prepared. One crystallises at 0° in forms apparently belonging to the orthorhombic system. These crystals exert a strong action on polarised light. A second solidifies at −8°, but may remain in a superfused condition to −25°. The third does not solidify at −55°. The author promises details concerning the properties and dissociation tensions of these compounds. C. H. B.

Density of the Vapour of Ammonium Dihydrosulphide. By H. St. Claire-Deville (*Compt. rend.*, **88**, 1239—1240).—The details of a determination referred to by Engel and Moitessier (*ibid.*, **88**, 1201—1203) are given. The author states that he has not succeeded in again preparing the neutral hydrosulphide used in this experiment. The density of the dihydrosulphide is 0·88 (air = 1). C. H. B.

Action of Aqueous Vapour on Carbonic Oxide in presence of Red-hot Platinum. By J. Coquillion (*Compt. rend.*, **88**, 1204).—A sample of gas from a Siemens gas generator had the composition CO_2, 5·00; CO, 29·75; H, 7·66; N, 57·59. After removal of the carbonic anhydride the gas occupied 95 vols. When it was saturated with aqueous vapour, and passed repeatedly over a red-hot spiral of platinum, the volume increased to 99. After treatment with potash, the gas occupied the original volume, 95. This process was repeated several times. The increase in volume was not constant, but depended on the duration of the experiment and the temperature of the platinum. The residual gas, after treatment with potash, always occupied 95 volumes. Analysis showed that this residual gas contained only a small quantity of carbonic oxide, the remainder being replaced by an equal volume of hydrogen. Under the influence of the red-hot

platinum, carbonic oxide and aqueous vapour give carbonic anhydride and free hydrogen. 100 volumes of pure carbonic oxide, saturated with aqueous vapour, were increased to 130 vols.: hence a state of equilibrium was reached when the gas had the composition CO_2, 30; H, 30; CO, 70; = 130. These experiments explain the fact, that in a Siemens gas generator, the carbonic anhydride is never entirely converted into monoxide. C. H. B.

Ammonium Nitrite and the Bye-products obtained in the Ozonisation of Air by Moist Phosphorus. By A. R. Leeds (*Chem. News*, **40**, 70—74).—Sterry Hunt, as long ago as 1848, threw out the suggestion that the nitrogen of the atmosphere is really composed of two equivalents (atoms) of the element, sustaining towards each other the same relations as the two equivalents (atoms) in nitrous oxide. Schaeffer appears to have arrived at a similar conclusion concerning the dual nature of nitrogen, and holds Hunt's view, that it is the nitryl of ammonium nitrite, and capable of forming this body by assuming again the elements of water. In 1862 Schönbein published an extensive series of experiments on the generation of ammonium nitrite from water and atmospheric air under the influence of heat. In none of these experiments, however, was the precaution apparently taken to use air which had been purified from its pre-existing ammoniacal and nitrous compounds. In repeating these experiments Carius employed most elaborate precautions, using only air and water which had been most carefully purified. The water was evaporated both with a rapid and with a slow change of atmosphere, at various temperatures, from the ordinary temperature of the air to 100°, both alone and after addition of baryta, the latter being devoid of nitrogen compounds, in contact with platinum spirals, and diffused over a great surface of purified cotton-wool, but in no case was ammonium nitrite formed. In such experiments therefore it is of the highest importance to exclude the possibility of the formation of ammonium nitrite and nitrous compounds from any extraneous sources. In cases of rapid oxidation, like the combustion of hydrocarbons, fats, phosphorus and other bodies in the air, if it be true that ammonium nitrite is formed, irrespective of any nitrogen compounds pre-existing in the atmosphere, the origin of this ammonium nitrite is to be looked for in other causes than the conjunction of atmospheric air and water-vapour under the influence of heat. The same remark applies if any ammonium nitrite is formed by the slow oxidation of phosphorus in contact with air and water.

Quite independently of the work done by other observers, an extended series of experiments was instituted by the author upon the phenomena which accompanied the ozonisation of air by means of phosphorus. In the earlier trials, attention was limited to the question whether oxidised compounds of nitrogen were produced or not. Subsequently, the research was made to include all other bye-products. It was deemed important to purify and measure the air used and the ozone formed, to determine the amount of phosphorus consumed and of phosphoric and phosphorous acids produced, and in case they were really present and it were possible to estimate them, the amounts of

nitrogen compounds, of hydrogen peroxide and ozone, remaining in solution in the jar- and wash-waters.

The phosphorus ozonator described in the Journal of the American Chemical Society, vol. i, p. 8, was employed throughout the whole course of this investigation. The most important result which the author appears to have arrived at is that the chief bye-product of the ozonisation of moist air by phosphorus is not phosphorous acid but phosphoric acid. It is generally stated that the former of these two substances is the one principally formed under these circumstances. This may be true in the sense that the phosphorous acid is first formed and that it is gradually transformed into phosphoric acid under the influence of nascent ozone. The author could not determine this point very readily in the course of these experiments. It is certainly an error to ascribe, as is done in various text-books, the dense white fumes seen in the ozonising chambers to ammonium nitrite—they are chiefly due to phosphoric anhydride.

The author's experiments do not permit him to say that no ammonium nitrite was formed during any period of the ozonisation; they prove merely that no ammonium nitrite could be detected at its close. If therefore this body were produced, it must have become oxidised to ammonium nitrate.

As to the cause of the formation of ozone itself under these circumstances, it may be conjectured, with Lamont and others, that it is connected with the uneven quantivalence of the elements taking part in the reaction, which may be represented by the equation $P_4 + O_{14} = P_2O_3 + P_2O_5 + 2O_3$. If this be true, we should anticipate the development of ozone whenever oxidation of a perissad occurred at temperatures compatible with the stability of the ozone molecule. In entering into new combinations, the oxygen molecules must undergo temporary resolution into their constituent atoms. These, while in the course of taking up new positions in other combinations, and animated by their atomic energy or energy of the nascent state, may either oxidise the oxygen molecule, or the nitrogen, or the molecule of water. In the first case, ozone would be produced; in the second, regarding water as the basic body and NNO as the nitryl, there might be formed, as Hunt has indicated, ammonium nitrate; in the third, hydrogen peroxide. D. B.

Nitrogen Iodide. By J. W. Mallet (*Chem. News*, **39**, 257).—The formula assigned to the highly explosive black substance formed by the addition of iodine to ammonia by various investigators are very different. Colin and Gay-Lussac ascribed to the formula NI_2, whilst six other eminent chemists stated that it contained hydrogen in different amounts, giving the following formulæ, NHI_2, NH_2I, NH_3NI_3, NH_34NI_3.

The author states that these erroneous formulæ have been given owing to want of sufficient attention to the unstable nature of the compound. The powder decomposes during drying at ordinary temperatures and in contact with water, nitrogen and iodine being liberated and IO_5 and hydriodic acids or ammonium salts formed.

The author prepared his compound by dissolving iodine in alcohol

and precipitating with water to get it into a fine state of division; this was then triturated in a mortar with the strongest aqueous ammonia at 0° C., the supernatant liquor poured off, and the black powder washed several times with the strongest aqueous ammonia; it was then washed first with alcohol of 95 per cent., then with absolute alcohol, and lastly with anhydrous ether, the temperature being kept at 0°; the powder was then transferred to a filter, and the remainder of the ether evaporated in a current of cold air. The product thus prepared was explosive in the highest degree, and in two instances it exploded under water with great violence.

The relative quantities of nitrogen and iodine contained in the substance were ascertained by decomposing an unweighed quantity of it by a moderately strong solution of sodium sulphite neutralised by dilute soda-ley and determining in equal volumes of the liquid the nitrogen as ammonia by mixing with excess of soda and boiling into a standard solution of sulphuric acid and the iodine as silver iodide.

A. The composition of the product prepared as above mentioned was thus found to agree with the formula NI_3.

B. Another product was prepared as above, with the exception however that a weaker ammonia solution was used and the temperature was not attended to. Its composition agreed with the formula as an average of the results obtained of 2·54 atoms of iodine to 1 of nitrogen.

C. Another sample, washed with water until free from ammonia and then left under water for two or three days and dried after washing with alcohol and ether as above described, gave an average of 2·09 atoms of iodine for each atom of nitrogen.

From these results the author proves that the nitrogen iodide, NI_3, can be obtained free from hydrogen, and goes on to show how, assuming the mixtures produced by the methods *B* and *C* to be definite compounds, they might be made to agree with the formulæ given to these products by other chemists.

From the *American Chemical Journal*. W. T.

Phosphorus Sulphides. By G. Ramme (*Deut. Chem. Ges. Ber.*, **12**, 1350—1351).—The liquid sulphides of phosphorus are decomposed on distillation with water. By the action of water at 150° on the sulphide P_3S_6, phosphorous, phosphoric, and hydrosulphuric acids are formed. The compound P_4S_3 can be obtained by heating a mixture of sulphur and red phosphorus in a tube at 260°, or by heating P_3S_6 with common phosphorus in a current of carbonic anhydride at 320°. This substance is freely soluble in carbon bisulphide. On evaporating the solution, pale yellow prisms (m. p. 166°) are deposited.

W. C. W.

Chemical Constitution of the Amalgams of the Alkali Metals. By Berthelot (*Compt. rend.*, **88**, 1335—1340).—In examining the chemical constitution of the liquid and solid amalgams of the alkali metals, the author treats them with dilute hydrochloric acid and measures the heat disengaged by the reactions, and also analyses the solution to determine definitely the quantity of alkali metals pre-

sent. From the results obtained, he deduces the heat of formation of the different bodies.

For one equivalent of potassium, the heat of formation first increases with a corresponding decrease in the number of mercury molecules until a maximum is reached, when it begins to decrease. The maximum heat of formation, 34·2, corresponds with a crystalline amalgam containing 1·6 per cent. potassium, and having the formula $Hg_{24}K$. The number of mercury molecules being so large renders it probable that it plays a part analogous to that of water in the saline hydrates. The liquid amalgams may be considered as solutions of the preceding body in mercury. No other crystalline amalgam has yet been obtained, but the heats of formation show the existence of several other compounds of such a nature.

The heats of formation of the sodium-amalgam follow a similar order to those of potassium, that containing about 2 per cent. of sodium possessing the highest, 21·1, which correspond with the formula $Hg_{12}Na$. The existence of other compounds can be shown, but not their composition.

The heat of oxidation of the amalgams rich in potassium, exceeds that of those rich in sodium, as do also the heats of formation. Thus the difference is +8·6 for $Hg_{12}K$ compared with $Hg_{12}Na$, and for $Hg_{24}K$ compared with $Hg_{12}Na$ + 12·6, whilst the heat of oxidation of potassium only exceeds that of sodium by +4·7. Therefore under similar conditions, the heat of oxidation of potassium can be reduced to + 48 cal. and that of sodium to +56 cal., that is to say, the relative affinities of the free alkali-metals for oxygen are inverted in this amalgam. This explains the apparent anomaly observed by Kraut and Popp, that sodium displaces the potassium in solution of potash when it is treated with sodium amalgam, the final result being the formation of the crystalline amalgam, $Hg_{24}K$. L. T. O'S.

Zinc and Cadmium Arsenates. By W. Demel (*Deut. Chem. Ges. Ber.*, **12**, 1279—1282).—An aqueous solution of arsenic acid dissolves zinc oxide, and on concentrating the solution a salt separates out in leaflets; the mother-liquors yield a further quantity in needle-shaped crystals, and the residual solution on addition of alcohol gives a white precipitate of the same salt. The salt washed with ether and dried over sulphuric acid gave analytical results corresponding with the formula $2ZnO.As_2O_5.H_2O + 2H_2O$, or $OH.AsO_3Zn + H_2O$.

This salt, by treatment with water, forms another crystalline body having the composition $10ZnO.4As_2O_5.10H_2O$. Both these arsenates dissolve easily in hydrochloric acid, and the solution so obtained gives a white precipitate when treated with an alkali. The precipitate is zinc arsenate, $3ZnO.As_2O_5 + 3H_2O$, also obtained by treating zinc sulphate with sodic arsenate (Salkowski, *J. pr. Chem.*, **104**, 162).

By using cadmium carbonate, analogous salts were obtained; first, acid cadmium arsenate, $2CdO.As_2O_5.H_2O + 2H_2O$, crystallising in shining needles; secondly, the salt $10CdO.4As_2O_510H_2O$, as a white crystalline compound; and finally, cadmium arsenate, $6CdO.2As_2O_5 + 3H_2O$, as a white voluminous precipitate. P. P. B.

A Compound of Alumina with Carbonic Acid. By URBAIN and RENOUL (*Compt. rend.*, **88**, 1133—1135).—When a salt of aluminium is precipitated by sodium carbonate, the precipitate is gelatinous and transparent if the solutions have been mixed at the boiling temperature; but if they are mixed at ordinary temperatures the precipitate is opaque, and when dried it is pulverulent and perfectly white. The former becomes hard and horny-looking by drying, and dissolves in acid only slowly and without disengagement of gas. The latter, on the contrary, dissolves immediately and with an abundant disengagement of carbonic acid gas. This gas is not due to the compound of soda, aluminium, and carbonic acid already known, nor to adhering sodium carbonate. The precipitate, after having been dried over sulphuric acid, had the percentage composition: alumina, 52; carbonic acid, 11; water, 37; which nearly corresponds with—

$$CO_2.2Al_2O_3.8H_2O,$$

that of a hydrated sub-carbonate. This compound is decomposed by heat, beginning to lose its carbonic acid at 30°, and parting with it completely after exposure for some time to a temperature of 100°.

R. R.

Ultramarine. By A. RINNE (*Deut. Chem. Ges. Ber.*, **12**, 1323—1326).—In the preparation of ultramarine, the product obtained from the same mixture of ingredients may vary in colour from green to deep blue.

If the different samples are washed with water, and the amount of sodium sulphate determined in the liquid, it will be found that the sodium sulphate increases with the intensity of the blue: *e.g.*, from green ultramarine, 2·41 per cent. Na_2SO_4, and from blue ultramarine, 6·87 per cent. Na_2SO_4 were obtained.

The amount of sulphuretted hydrogen evolved when the ultramarine is treated with an acid is less for blue than for green ultramarine, *e.g.*, green = 1·96, blue 0·22 per cent. S. Since ultramarine contains sodium thiosulphate and sulphite, these numbers do not prove that the blue ultramarine contains but a very small quantity of sodium sulphide; they merely indicate that the sulphuretted hydrogen evolved from the decomposition of the sodium sulphide is almost completely destroyed by the sulphurous anhydride which is liberated from the sulphur oxy-acids.

The author regards ultramarine as a sodium-aluminium silicate in which varying quantities of sodium sulphide and the sodium salts of sulphur oxy-acids are dissolved. W. C. W.

Red and Yellow Ultramarine. By E. W. BÜCHNER (*Dingl. polyt. J.*, **231**, 466).—In the production of ultramarine in muffle furnaces, red and yellow ultramarine colours are often produced. These the author says are due both to a suppressed formation of the ultramarine on the one hand, and to over-heating on the other.

On analysis of the red in comparison with the blue, it will be seen that the former contains a smaller proportion of sodium and a larger proportion of alumina residuum than the latter. In the case of the red, the heat does not seem to have been sufficient to flux the alumina completely.

			Reckoned to the 100 parts of Al_2O_3.	
	Blue.	Red.	Blue.	Red.
SiO_2	39·12	37·81	164·6	152·3
Alumina residuum	6·92	9·01	29·1	36·3
S	11·67	10·89	49·1	43·8
Na	14·31	12·68	60·2	51·1
Al_2O_3	23·76	24·82	100·0	100·0
Salts which may be washed out			14·70	33·23

The red and yellow colours are produced most beautifully on overheating, but strange to say, only as a moderately strong blush where the heat must necessarily have been greatest.

It is well known that when the temperature rises very high in ultramarine furnaces, sulphuric anhydride is liberated, and thinking this might be the cause of the change in the blue colour, the author made an experiment by taking ready prepared ultramarine, heating it to a temperature of 350° to 400°, and passing over it sulphuric anhydride vapours. The colour of the ultramarine changed first to violet then to red, and lastly to yellow.

He further experimented by passing chlorine at 410° over completely formed ultramarine, and found that it changed rapidly to violet, red, and lastly to a beautiful lemon-yellow colour. When the chlorine was passing he observed a dense white vapour which came off into the receiver which contained water; these fumes he assumed to be sulphuric anhydride, resulting from the action of the chlorine on the mass, but on testing the water in the receiver, he found it to be free from sulphuric acid.

The red and yellow ultramarine so formed were found to contain chlorine, but no salt of sulphuric acid.

As it was possible that the presence of chlorine prevented the sulphuric anhydride from being absorbed, strong potash solution was substituted for it, and the presence of sulphuric acid could then be detected in the potash solution. He attributes the change in colour to the direct action of the sulphuric anhydride brought about by the indirect action of the chlorine.

To study this action further, chlorine was passed over sodium sulphate, heated in the same way as the ultramarine, but no sulphuric anhydride was evolved, from which it would appear that the sulphur played an important part in the action.

Leltner, of Nürnberg (*ibid.*, **230**, 500), obtained a patent for the manufacture of red ultramarine by passing chlorine gas and steam over ultramarine blue at a high temperature, and he designates his product a hydroxylated ultramarine, but as the author has produced the red without the use of steam, he considers Leltner's appellation to have been given on an erroneous basis.

The author further states that on analysis the blue was found to contain more sodium than the red, and the red more than the yellow,

and he has actually succeeded in producing red and yellow ultramarines by employing a smaller quantity of sodium in the ultramarine mixture.

The author considers that none of the ultramarine colours except the blue can have any practical value. W. T.

Peculiarity of an Experiment of Gay-Lussac and Thenard. By H. Debray (*Compt. rend.*, **88**, 1340—1342).—Gay-Lussac and Thenard in their researches on the alkali-metals, pointed out that when the vapour of caustic soda or potash is passed over red hot metallic iron, the oxygen set free by the reduction unites with the iron contained in the part of the tube without the furnace, whilst the iron directly heated is not attacked. The explanation is seen from the researches of Deville (*ibid.*, **70**, 1165—1201, and **71**, 3), in which he points out that if a mass of partially oxidised iron be unequally heated in an atmosphere containing more or less hydrogen, the oxygen is expelled from the hottest portion and unites with the cooler. This is borne out by the author's experiments. A boat containing magnetic oxide of iron is placed in a tube with another boat containing some metallic iron reduced by hydrogen, the ends of which touch. The first of these is heated directly in a furnace, whilst the other receives heat by conduction from the furnace. The hydrogen retained by the reduced iron is expelled, the oxide is reduced, and the metal in the end of the boat farthest from the source of heat is oxidised.

L. T. O'S.

Iron Reduced by Hydrogen. By H. Moissan (*Compt. rend.*, **89**, 176).—The author finds that many samples of the reduced iron used in pharmacy are mixtures of metallic iron with protoxide and magnetic oxide, which impart a black colour. They also contain sulphur and, in some cases, small quantities of arsenic, copper, silica, and soluble salts. In order to obtain a good product, the current of hydrogen should be somewhat rapid, and perfectly dry, the temperature uniform, and the passage of the gas should be continued for a considerable length of time. C. H. B.

A New Double Salt of Chromic Acid, $K_2CrO_4.Fe_2(CrO_4)_3.4H_2O$. By C. Hengsen (*Deut. Chem. Ges. Ber.*, **12**, 1300—1303).—If the precipitate, produced when concentrated solutions of potassium chromate and ferric chloride are mixed, is dissolved in hydrochloric acid, the acid solution will slowly deposit a dark red leafy crystalline mass. The substance is rapidly washed with cold water, or with alcohol and ether. It decomposes when left in contact with water for any length of time. W. C. W.

Solution of Carbonic Oxide in an Acid Solution of Cuprous Chloride. By H. Hammerl (*Compt. rend.*, **89**, 97—98).—An acid solution of cuprous chloride containing Cu_2Cl_2 14·015 per cent. HCl 18·64 per cent., and H_2O 67·345 per cent., dissolves 20 times its volume of carbonic oxide before the crystalline compound discovered by Berthelot begins to be formed. This solution has the sp. gr. 0·642 at 16°, and the heat evolved in the solution of 1 mol. = 2 grams of the

gas is +11·37 cal.; the heat evolved by the solution of carbonic anhydride (44 grams) in water, is 5·6 cal., or about one-half. The crystalline compound has the composition $Cu_2Cl_2.CO.2H_2O$, and its heat of formation is ascertained by determining the total heat evolved by the solution of the carbonic oxide, and the formation of the compound; this is 14·82. The difference between this number, 14·82, and the heat evolved by the solution of the gas gives $14·82 - 11·37 = 3·45$, the heat of formation of $Cu_2Cl_2.CO.2H_2O$. L. T. O'S.

Grey Modification of Tin. By A. Schertel (*J. pr. Chem.* [2], **19**, 322—326).—A box containing rings and metals was recently discovered in a niche in Freiberg Cathedral, where it must have lain for three or four hundred years. One of the rings was made of almost pure tin, containing only traces of iron and sulphur. The tin, which easily crumbled between the fingers, was of a reddish-grey colour, and uneven fracture; sp. gr. at 19° = 5·8 (ordinary tin = 7·3). When heated in vapour of acetone (59°) it was converted into ordinary tin. The grey modification of tin was found to be electronegative towards ordinary tin when immersed in dilute potash, hydrochloric or sulphuric acid, but electropositive when in dilute nitric acid.

Five tin rings, possessed of all the characters of the ordinary metal, were found in the same box. M. M. P. M.

Solubility of Stannic Oxide in Hydrochloric Acid. By A. E. Arnold (*Chem. News*, **40**, 25).—When cassiterite in fine powder, or strongly ignited stannic hydrate, is digested with strong hydrochloric acid at 100°, a very perceptible quantity of tin enters into solution as stannic salt. The action takes place more energetically above the boiling point of water, when the dioxide is heated in a current of hydrochloric acid gas. In the complete analysis of cassiterites, therefore, this fact should be borne in mind. As an example, there was found in a specimen of the mineral :—

Stannic oxide, insoluble ..	38·49 per cent.
„ „ soluble	0·06 „

The stannic oxide in a few rare minerals is soluble to a considerable extent in dilute hydrochloric acid, evidently owing to the presence of a stannate of some basic oxide.

These results are noteworthy, inasmuch as there appears to be a considerable amount of uncertainty concerning the solubility of natural stannic oxide, and of that artificially prepared, in hydrochloric acid. D. B.

Tungsten Oxychlorides and Chlorides. By H. Schiff (*Liebig's Annalen*, **197**, 185—193).—According to Teclu (*ibid.*, **187**, 255), when phosphorus pentachloride is heated with tungstic acid in sealed tubes at 170°, tungsten hexachloride is the only product. This he regards as not in accordance with the previous results of the author (*ibid.*, **102**, 111). The author in conjunction with A. Piretti has repeated his experiments, and finds that, when tungstic acid is heated in a retort with 1—2 mol. phosphorus pentachloride, phos-

phorus oxychloride, the two tungsten oxychlorides WO_2Cl_2 and $WOCl_4$, and a small quantity of tungsten hexachloride are formed. The chief product is $WOCl_4$, which results from the first formed WO_2Cl_2 being resolved by heat into $WOCl_4$ and WO_3, thus: $2WO_2Cl_2 = WO_3 + WOCl_4$. That this is the case is shown by the fact that the oxytetrachloride is the chief product of phosphorus pentachloride on sodium tungstate, these bodies reacting at first thus: $WO_4Na_2 + 2PCl_5 = 2POCl_3 + 2NaCl + WO_2Cl_2$. Further, the oxytetrachloride when heated in sealed tubes at 170° with phosphorus pentachloride, is decomposed, yielding tungsten hexachloride as follows:—$WOCl_4 + PCl_5 = POCl_3 + WCl_6$. These observations show that Teclu's results (*loc. cit.*) are due to the conditions of his experiment. That tungsten oxychlorides are acted on by phosphorus pentachloride at low temperatures under high pressure, is shown by the fact that when a solution of this latter body in carbon bisulphide is sealed up with tungstic acid and the mixture allowed to stand some days at 30—40°, and then heated to 80—90°, a mixture of tungsten oxychlorides results, together with tungsten hexa- and penta-chlorides. The latter is produced by the decomposition of the hexachloride, the liberated chlorine reacting with the carbon bisulphide, and forming sulphur chloride.

P. P. B.

Formation of Mercuric from Mercurous Chloride. By G. Vulpius (*Arch. Pharm.* [3], **14**, 347).—Experiments were instituted to determine whether the statement that calomel under the influence of cane-sugar and lime yielded mercuric chloride was correct, with the following results:—No mercuric chloride was produced in 24 hours from mixtures of calomel with sugar, milk-sugar, magnesia usta, sodium bicarbonate: after three months the result was the same: traces of mercuric chloride were detected after three months in a mixture of calomel, milk sugar, and sodium bicarbonate; considerable quantities were produced when cane-sugar and sodium bicarbonate were present, together with moisture: digestion with water produced the change only when magnesia usta or sodium bicarbonate was present.

E. W. P.

Mercuric Iodide. By H. Köhler (*Deut. Chem. Ges. Ber.*, **12**, 1234—1236).—The author defends the correctness of his determination of the melting point of mercuric iodide (this vol., 602), and replies to the remarks of Kraut (*Ber.*, **12**, 1076).

P. P. B.

Alloys of Lead and Antimony. By F. de Jussieu (*Compt. rend.*, **38**, 1321—1322).—These alloys are obtained by adding antimony to red-hot lead. They fuse at about 355°, and do not give off vapours, even when heated to redness. They are soluble in molten lead, and crystallise by liquation in the rhombohedral system. These alloys decompose easily, an alloy richer in antimony being formed, and some of the lead set free. They show a great tendency to assume a superfused condition.

C. H. B.

Samarium, a New Metal from Samarskite. By L. de Boisbaudran (*Compt. rend.*, **89**, 212—214).—The solution of an oxide

extracted from samarskite gave a pair of absorption-bands in the blue at 480° and 463·5°, and another pair in the violet at 417° and 400·75°. In both pairs, the most refrangible band is the narrower and more intense of the two. These bands are not identical with those of decipium, recently described by Delafontaine, or of any other known substances, and indicate the existence of a new metal to which the author gives the name *Samarium*. The bands 417° and 400·75° were observed some time ago by Soret (*Compt. rend.*, 1878).

C. H. B.

Norwegium, a New Metal. By T. Dahll (*Chem. News*, **40**, 25). This metal has been detected and isolated by the author in a sample of copper-nickel from the Kragerö, Skjœrgoarden. The colour of the pure metal is white, with a slight brownish cast. When polished it has a perfect metallic lustre, but after a time it becomes covered with a film of oxide. Its hardness is equal to that of copper, its melting point is 350°. Its equivalent appears to be 145·9°. Only one oxide, NgO, has been obtained. Its sulphide has a brown colour, and is soluble in ammonium sulphide. With a slight addition of potassium ferrocyanide, it gives a brown, but with larger proportions a green precipitate. The sulphuric solution is turned brown on addition of zinc, the metal being deposited in a pulverulent form. The solutions of this metal are blue, but become green on dilution. The author is continuing his studies of this new substance. D. B.

A New Metal discovered by T. Dahll. By Hiortdahl (*Compt. rend.*, **89**, 47—48).—This metal was found in a mineral composed of arsenide of nickel and nickel-glance, from Oterö, a small island near Kragerö. The mineral is roasted to expel sulphur and arsenic, and the roasted ore dissolved in an acid, and precipitated with sulphuretted hydrogen: the precipitate is washed free from nickel and roasted, when it leaves a residue consisting of the oxide of the new metal, which the discoverer calls *Norwegium*. The oxide is dissolved in *aqua regia*, and precipitated with potash (avoiding excess) as hydrate, of an emerald-green colour. This is readily reduced by hydrogen, yielding a white, malleable metal, about as hard as copper, and melting at a dull red heat. Its sp. gr. is 9·44, and it dissolves with difficulty in hydrochloric acid, but readily in nitric acid, giving a blue solution which turns green when diluted with water; it also dissolves in sulphuric acid. Two specimens of oxide from different preparations, when reduced in a current of hydrogen, gave 9·6 and 10·15 per cent. of oxygen, which gives Ng = 145·95, the oxide being NgO.

With potash, ammonia, and carbonate of soda, it gives green precipitates, which are soluble in excess of the reagents, yielding blue solutions. Sulphuretted hydrogen, even in strongly acid solutions, gives a brown precipitate of sulphide insoluble in ammonium sulphide. In the oxidising flame it gives, with borax, a bead yellowish-green when hot, blue when cold; and a blue bead in the reducing flame. With microcosmic salt it gives a yellow bead when hot, which on cooling changes, first to emerald-green, then violet, and finally to blue. It is reduced to the metallic state with sodium bicarbonate on charcoal. L. T. O'S.

Mineralogical Chemistry.

A New and Remarkable Mineral Locality in Fairfield Co., Connecticut, U.S.A., with a Description of several New Species occurring there. By G. J. Brush and E. S. Dana (*Amer. J. Sci.* [3], **16**, 114—123, continued from p. 46).*—*Dickinsonite.*—This mineral occurs in foliated crystalline masses, also lamellar-radiated, and sometimes stellated. The massive variety forms the gangue to eosphorite and triploïdite; distinct crystals are rare. Hardness = 3·5—4, sp. gr. 3·338—3·343. Lustre vitreous, on the cleavage face pearly. Colour of the crystals, oil- to olive-green; of the massive variety, grass-green, and sometimes dark. Streak, nearly white; transparent to translucent; laminæ brittle; fracture uneven; basal cleavage perfect.

Dickinsonite crystallises in the monoclinic system; the principal angles are as follows:—Plane angle of the base = 120° 0′, 0P : $\infty\breve{P}\infty$ = 61° 30′, 0P : $\infty\breve{P}3$ = 42° 30′. The axial ratio is c (vert.) : b : a' = 0·6917 : 0·5773 : 1·0000. Observed planes 0P, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, −P, −2P, $3\breve{P}\infty$. It will thus be seen that dickinsonite is crystallographically analogous to the micas and chlorites. The cleavage-plates show a marked dichroism parallel to the edge 0P : $\infty\breve{P}\infty$. Two analyses gave the following results, after deduction of admixed quartz and eosphorite:—

P_2O_5.	FeO.	MnO.	CaO.	Li_2O.	K_2O.	Na_2O.	H_2O.	
39·36	12·40	25·10	13·36	0·03	0·89	5·25	3·86	= 100·25
39·53	11·90	23·96	14·98	0·24	0·73	4·78	3·88	= 100·00

In the second analysis the lime was determined by difference.

The numbers lead to the formula, $R_3P_2O_8 + \frac{3}{4}H_2O$, where R = Mn, Fe, Ca, Na = 5 : $2\frac{1}{2}$: 3 : $1\frac{1}{2}$.

In the closed tube, dickinsonite gives off water, and leaves a magnetic residue. Before the blowpipe, it fuses and colours the flame first green and then greenish-yellow. Dissolves in the fluxes, giving reactions for iron and manganese. Soluble in acids.

Lithiophilite.—This mineral is found imbedded in albite in lumps from one to three inches in diameter, generally thickly coated with a black mineral, a product of its oxidation. No crystals were found. The hardness is about 4·5, sp. gr. 3·424—3·432.

Colour of the unaltered mineral, bright salmon colour or honey-yellow, sometimes yellowish-brown to dark umber-brown. Fracture uneven to subconchoidal; lustre vitreous to resinous; translucent and transparent in small splinters.

The optic axes lie in the basal section, the acute bisectrix being normal to the brachypinacoïd. The axial angle is very large = 74° 45′ (for red rays), and 79° 30′ (for blue rays). The dispersion of the axes is strong $v > \rho$. Character of the double refraction positive. The mean composition is as follows:—

* This vol., p. 20.

P_2O_5.	MnO.	FeO.	Li_2O.	Na_2O.	H_2O.	SiO_2.
44·67	40·86	4·02	8·63	0·14	0·82	0·64 = 99·78

leading to the formula $LiMnPO_4$ or $Li_3PO_4 + Mn_3P_2O_8$, analogous to that of triphylite.

Heated in a closed tube, lithiophilite gives off water, turns dark brown and fuses, but does not become magnetic. Before the blowpipe it fuses, colouring the flame deep red, streaked with pale green on the lower edge. With borax, &c., it gives in the outer flame a deep amethyst bead, and in the inner flame a faint reaction for iron. It is soluble in acids.

Reddingite.—This comparatively rare mineral generally occurs massive, rarely in minute octohedral crystals, belonging to the orthorhombic system. Hardness = 3—3·5; sp. gr. (of the pure mineral) = 3·102. Lustre vitreous to sub-resinous; colour pale rose-pink to yellowish-white, sometimes dark brown from surface alteration, streak white. Transparent to translucent; brittle; fracture uneven; cleavage distinct in one plane, whose direction could not be ascertained.

Distinct crystals of reddingite are rare, occurring only in cavities in the massive mineral. They are always octohedral in habit, sometimes only the unit-pyramid is present, and in other cases a second macrodiagonal pyramid. Axial ratio, c (vert.) : $\bar{b}$: $\breve{a}$ = 1·0930 : 1·1524 : 1·0000. Observed planes $\infty\breve{P}\infty$, P, $\bar{P}2$.

The mean chemical composition of reddingite (from two analyses) after deduction of admixed quartz is :—

P_2O_5.	MnO.	FeO.	Na_2O.	Li_2O.	CaO.	H_2O.
34·52	46·29	5·43	0·31	trace	0·78	13·08 = 100·41

leading to the formula $Mn_3P_2O_8 + 3H_2O$; which is the same as that found by Debray (*Ann. Chim. Phys.* [3], **61**, 433) for an artificial salt which he obtained by boiling manganous carbonate with excess of phosphoric acid.

Reddingite corresponds closely with scorodite and strengite in crystalline form and chemical composition. On heating reddingite, it first whitens and gives off water, then turns yellow and brown. Before the blowpipe, it colours the flame green, and melts easily to a black non-magnetic globule. Dissolves in borax, &c., giving the reactions for manganese and iron. It is soluble in hydrochloric and nitric acids.

Fairfieldite.—This is a yellowish-white to colourless mineral, having an adamantine lustre on the cleavage surface. Hardness = 3·51. Sp. gr. = 3·15. It has the composition of a hydrous silicate of manganese and lime, $R_3P_2O_8 + 2H_2O$, [R = Mn″ and Ca with small quantities of iron and soda]. A further description of this mineral will be given in a future paper. C. W. W.

The Native Iron of Greenland and the Dolerite which encloses it. By J. L. Smith (*Ann. Chim. Phys.* [5], **17**, 452—505).—In 1870 Nordenskjöld discovered on the seashore at Ovifak, in the Island of Disko, large masses of native iron lying between high and low water level, amongst rounded blocks of granite and gneiss at the

foot of a basaltic cliff, from which rise the horizontal beds of trass and dolerite, of which Mount Ovifak is composed. In a space of 50 square metres 20 masses of iron, and basalt enclosing iron, were found, varying in weight from 1 kilo. to 21,000 kilos. 16 metres distant from the largest block was found a dyke of basalt, enclosing lenticular masses of nickeliferous iron. These masses were separated from the basalt by a thin coating of oxide, which sometimes contained hisingerite. They resembled meteoric iron in composition, and in the resistance which they offered to the action of the air. The author has examined these and similar masses from other localities, with a view to determine whether they are of terrestrial or extraterrestrial origin.

The Island of Disko consists of beds of the miocene formation, resting on beds of gneiss. The miocene beds contain many layers of lignite and fossil plants, and are traversed by beds and dykes of basalt. The carbonaceous matter in the immediate neighbourhood of the basalt is converted into graphite. The basalt contains metallic iron in large elliptical masses, in small balls and fine particles, and sometimes in the form of small veins.

The specimens found at Ovifak may be divided into five classes:—

(1.) Large irregular masses, having an elongated form. The surface was of a deep brown colour, with here and there points possessing a metallic lustre. One mass weighing 5 kilos. was sawn in two. The exterior crust was very hard, but the interior consisted of a soft mixture of metallic iron and oxide of iron, which could be cut with a knife. On exposure to the air the whole mass rapidly disintegrated. The hard crust had the following composition:—Fe_2O_3, 76·21; Fe, 16·56; Ni, 1·08; Co, 0·48; Cu, 0·08; S, 1·12; P, 0·14; C, 1·36; H_2O, 4·50 = 101·53. Traces of lime, magnesia, and chlorine were also present. The sp. gr. of the substance was 5·0. The interior magma contained 22·32 per cent. Fe, 1·37 Ni, and 0·65 Co; in other respects its composition resembled that of the outer crust. It contained in addition small quantities of soluble sulphates and chlorides. The particles of metallic iron separated from the oxide by levigation had the composition, Fe, 93·16; Ni, 2·01; Co, 0·80; Cu, 0 12; P, 0·32; S, 0·41; Cl, 0·02; C (combined), 2·34 = 99·18; sp. gr. 6·42. No graphite was found.

(2.) Irregular, hard masses of malleable iron, found exclusively in the interior of the dolerite. Sp. gr. 7·46. Composition, Fe, 90·17; Ni, 6·50; Co, 0·79; Cu, 0·13; residue (SiO_2), 1·54 = 99·13.

(3.) Hard rounded nodules of varying dimensions, having a very crystalline fracture. Their polished surface exhibited brilliant dendritic markings. Analysis gave the following numbers: Fe, 88·13; Ni, 2·13; Co, 1·07; Cu, 0·48; P, 0·25; S, 0·36; Cl, 0·08; insoluble silicates, 4·20; C (combined), 2·33; Mg (traces) = 99·03. Sp. gr. 6·80.

(4.) Intimate mixtures of dolerite with varying quantities of metallic iron. Fracture not metallic except at small points. The polished surfaces exhibit metallic dendritic figures, consisting of fine lines crossing at all angles. This structure shows that the solidification of the iron must have been contemporaneous with the solidification of the rock in which it is enclosed. The dendritic markings

resemble Widmandstatt's figures. When the rock is powdered, and the iron separated by means of a magnet, it is found to have the same composition as that in Class (1). The dolerite possesses the average composition of the dolerite of the region. Mixed with the iron and the dolerite are thin scales of graphite, which may be separated by means of hydrofluoric acid, and give graphitic acid when treated in the usual manner.

(5.) Dolerite containing grains of malleable iron, more widely diffused than in Class (4). The largest grains are about the size of a pea. The dolerite has the composition SiO_2, 48·00; Al_2O_3, 12·20; FeO, 15·31; Fe_2O_3, 3·20; CaO, 9·70; MgO, 8·63; alkalis, 1·16; H_2O, 2·25 = 100·45. It encloses, in addition to metallic iron, graphite, spinelle, hisingerite, metallic sulphides, and corundum.

Two analyses of specimens of dolerites free from metallic iron, obtained from localities in Disko some distance from Ovifak, gave the following numbers:—(*a.*) SiO_2, 48·02; Al_2O_3, 15·06; Fe_2O_3, 6·50; FeO, 9·45; MnO, 0·12; MgO, 8·62; CaO, 9·52; Na_2O, 1·50; K_2O, 0·73; P, 0·06. (*b.*) SiO_2, 49·02; Al_2O_3, 13·11; Fe_2O_3, 5·03; FeO, 11·20; MnO, 0·20; MgO, 8·16; CaO, 10·10; Na_2O, 1·33; K_2O, 0·35, H_2O, 1·80. Both specimens contained traces of Ni and Co. They do not differ in composition from the dolerite containing metallic iron. Microscopical examination shows that the dolerite consists of augite and plagioclase (which further chemical examination proves to be labradorite and not anorthite), together with large rounded fragments of olivine, grains of magnetite, and flakes of viridite. Dolerites containing metallic iron from other localities in Greenland have a similar composition.

Minerals occurring with the metallic iron in the dolerite:—

Pyrrhotine or *pentlandite* occurs in masses varying from small grains to blocks of considerable size. It differs in appearance and structure from troïlite, which is found in large nodules in meteorites, and to which it has often been compared. Analysis gives the following numbers:—S, 38·38; Fe, 58·48; Ni, 1·05; Co, 0·55; Cu, 1·58; sp. gr. = 4·46. It is lighter than troïlite (sp. gr. 4·9), and much more magnetic. The author has compared many specimens of these two minerals, and is satisfied that the sulphide occurring with the metallic iron is pyrrhotine and not troïlite.

Hisingerite occurs in rounded concretions and small fragments of a deep green colour. It has evidently been produced by alteration of the dolerite, and varies in composition in different localities, more especially with regard to the amount of water present. An analysis of an average specimen gave the following result: SiO_2 30·04; Fe_2O_3, 57·12; H_2O, 10·89 = 98·05.

Corundum is found in the dolerite in small irregular grains, sometimes bluish-grey, sometimes rose-coloured. It contains traces of iron and magnesium, and generally accompanies graphite.

Magnetite, *spinelle*, and *graphite*, are also found in varying quantity. The graphite sometimes amounts to as much as 17·5 per cent. of the whole mass.

At a promontory near Assuk, 100 miles from Ovifak, the basalt cuts through a bed of coal, and is full of metallic iron. This basalt

resembles that of Ovifak in composition, but the particles of iron are more rounded and less angular. Many of them are surrounded by crystals of labradorite, which are probably sometimes mixed with oligoclase. At Igdlokungoak, in the same locality, M. Steenstrup found in a dyke of basalt an enormous block of nickeliferous pyrites occupying a volume of about 200 cubic feet, and weighing about 28,000 kilos. Analysis gave S, 36·85; Fe, 53·01; Cu, 2·43; Ni, 3·11; Co, 0·78; P, 0·42; insoluble residue, 3·20 = 99·38; sp. gr., 4·391. Traces of Al_2O_3, CaO, and MgO, were present. The pyrites is accompanied by crystallised ferrous carbonate.

The author has examined specimens of native iron from seven other localities on the north side of Greenland. They resemble in appearance and composition those found at Ovifak.

Origin of the Native Iron.—As previously stated, the native iron of Greenland resembles meteorites in appearance, and in containing considerable quantities of nickel and cobalt. If, however, we regard the native iron of Assuk as having a terrestrial origin, and from its position in the heart of a basaltic dyke we can scarcely do otherwise, the presence of nickel and cobalt loses its significance, since this iron contains both. The points of difference are numerous. True meteorites are solid throughout, and never possess a pasty interior like the specimens in Class (1). Unless altered by exposure they are fractured with difficulty, whereas many unaltered specimens of Greenland iron break with comparative ease. Then, too, the blocks of iron are found embedded in, and in immediate contact with, the dolerites of the locality. M. Tschermak supposed that they derive their origin from meteorites, consisting of eukrite (*i. e.*, a mixture of anorthite and augite), metallic iron, and troïlite, which fell into the basalt whilst it was still in a fused condition. He admits that graphite and magnetite, which accompany the Greenland iron, have never been found in eukritic meteorites. The author has shown that there is every reason to believe that the sulphide present is not troïlite, but pyrrhotine. He has also proved the absence of anorthite. Again, the mineral matter in immediate contact with the iron possesses the same composition as the mass of the rock. Hence the facts prove that the iron is not derived from eukritic meteorites. The author advances the following theory with regard to its formation. The dolerites containing the iron are, as previously stated, intrusive sheets and dykes, cutting through beds of lignite and other carbonaceous matter. The intense heat of the molten lava acting on the carbonaceous substances would disengage large quantities of gaseous hydrocarbons, which then acted upon the silicates, giving rise to metallic iron containing combined carbon. The reduction would be assisted by fragments of carbonaceous matter entangled in the dolerite. A portion of the carbon was at the same time converted into graphite. This theory is supported by the experiments of M. Daubrée, who, by fusing silicates such as peridote, hypersthene, basalt, and especially lherzolite from Prade, in a crucible lined with charcoal, obtained metallic iron analogous to that of Ovifak in appearance and chemical composition. A sample of iron obtained in this manner from peridote had the composition, Fe, 89·96; Mn, 0·66; Cr, 1·66; Ni, 1·16; Co

(sensible traces), Cu, 0·11; C (combined), 1·73; C (free), 2·61; Si, 2·30; S, traces; sp. gr. 6·955. C. H. B.

The Sulphur in Fossil Resin. By O. Helm (*Dingl. polyt. J.*, 231—477).—Thin slices of milk-white amber when magnified 200 to 500 times show very fine round closed bubbles, which are largest in bone-coloured amber. The bubble spaces are filled with water when the amber is fresh from the sea, but it gradually evaporates on warming.

When the water has evaporated by years of exposure to the air, the spaces again become filled with water when the dry amber is laid for a length of time in that liquid. Amber is consequently penetrable by water and air: in the same way, organic substances containing sulphur seem to be absorbed by the amber, for, according to the author, the amber contains 0·26 to 0·42 per cent. of sulphur, which is driven off when the amber is submitted to dry distillation. When, however, the resin is digested in alcohol or ether only a small proportion of the sulphur containing substances are dissolved.

Gedanite is a resin found along with amber, but which is distinguished from the latter by being less hard, of different solubility, and containing no succinic acid.

Its composition is C, 81·01; H, 11·41; O, 7·33; S, 0·25. The sulphur exists in combination in an organic substance.

A Syrian asphalte contained 0·19 per cent. of sulphuric acid, 0·16 per cent. of sulphur combined with iron, and 8·78 per cent. of sulphur in combination with organic substances.

An American asphalte contained 10·85 per cent. of sulphur in combination with an organic substance.

Ozokerite contains no sulphur. W. T.

Occurrence of a Solid Hydrocarbon in the Eruptive Rocks of New Jersey, U.S.A. By J. C. Russell (*Amer. J. Sci.*, **16**, 112—114). This mineral occurs in cavities in an amygdaloïd trap associated with the sheet of trap-rock known as the First Newark Mountain. The cavities in the amygdaloïdal rock are tubular, and from 3 to 4 inches long by a quarter of an inch in diameter. Sometimes these tubes are lined with a coating of quartz or calcite, a line or two in thickness, the remainder of the space being filled with a jet-black carbonaceous substance, closely resembling the albertite of New Brunswick. It is insoluble in acids and in alkalis, and almost, if not quite, insoluble in alcohol, ether, and oil of turpentine. It is infusible, but softens by heat, and burns with a yellow flame, emitting an agreeable odour, and leaving about 0·1 per cent. of its weight of ash.

The mineral is probably formed from petroleum by evaporation of the more volatile constituents, and subsequent partial oxidation of the remainder. No analyses of the mineral are given. C. W. W.

Artificial Formation of Coal. By E. Fremy (*Compt. rend.*, **88**, 1048—1054).—The experiments described in this paper had for their object the artificial formation of coal from vegetable matters. The author's former researches had enabled him to separate and distin-

guish various chemical principles, of which the framework of all vegetable structures is formed. Such are *vasculose*, *cutose*, and the different kinds of *cellulose*. The mode of operation consisted in heating the substances at 200° or 300° in closed tubes for many hours. Tissues formed of the principles above mentioned were the first subjects of experiment; they were found to have undergone a deep change, having become black and brittle, and they gave off water, gases, and tarry matters. Nevertheless, they showed no signs of fusion and retained their original organisation. The final products had, in short, no resemblance to coal.

Very different results were obtained when certain vegetable products, such as sugars, starch, gums, and chlorophyll, together with certain fatty resinous matters, were submitted to the same treatment, for long calcination under pressure transformed them into a substance having a certain analogy to coal. The products were black, glistening, often fused, absolutely insoluble in neutral acid or alkaline liquids. Yet the substances had not been converted into charcoal, for the products were true organic bodies capable of yielding when heated, water, gases, tars, and a residue of hard, lustrous coke. Analysis showed that in the proportions of carbon, hydrogen, and oxygen, these artificial coals bore the closest analogy to the natural mineral.

The examination of certain lignites and other fossils led the author to conclude that in the process of the natural transformation of plants into coal, the vegetable matters are, first of all, changed into peat, and that when they are brought into this form, the disappearance of the organised tissues is due to a kind of peaty fermentation. This hypothesis was confirmed by finding that ulmic acid from peat, or from other sources, yielded, by the prolonged influence of heat and pressure, a substance having the properties and composition of coal.

The mixture of chlorophyll, fatty matters, and resins, which alcohol extracts from leaves, yielded when heated under pressure for 50 hours, a black, viscous, odorous substance, insoluble in caustic alkalis, and having a strong resemblance to natural bitumens.

One general conclusion established by these results is, that although coal is an organic, it is not an organised substance. The impressions of vegetable structures sometimes seen in coal have been produced in the same way as similar impressions found in other minerals, that is to say, the impressions were moulded on the external forms of the plants, when originally the coal was a plastic bituminous matter.

R. R.

The Tellurium-ores of Siebenburgen (Transylvania). By A. Schrauf (*Jahrb. J. Min.*, 1878, 862—863).—Sylvanite occurs principally at Offenbanya, whilst nagyagite, manganese-spar (rhodochrosite), and bournonite, occur at Nagyag, the ores filling clefts in dacite at both places. The tellurium ores of Zalathna are found in a breccia-like rock, whilst those from Facebay are disseminated in hornstone.

Sylvanite.—The author corrects his former statements, and concludes that this mineral is monosymmetrical, with the axial relation $a : b : c = 1{\cdot}63394 : 1 : 1{\cdot}2653$. The crystals often exhibit many forms in combination, and are very complicated, $\infty P\infty$ predominating some-

times, or this form with $\infty\breve{P}\infty$; also $-\breve{P}\infty$, coupled with an ortho-diagonal form-development, whilst finally $+2\breve{P}2$ occurs sometimes very strongly developed. Twins are not uncommon, the twin-plane being a face of $-\breve{P}\infty$. The so-called graphic-tellurium occurs in twins, according to the same law.

Krennerite has the axial relation 3·93961 : 1 : 0·50733, according to Schrauf, and this agrees with that given by vom Rath (*Jahrb. f. Min.*, 1878, 825), whilst the following new forms were observed; viz., $3\breve{P}\infty.2\breve{P}\infty$.

Nagyagite.—The author believes this mineral to be rhombic, with the axial relation $a : b : c = 0{\cdot}2807 : 1 : 0{\cdot}2761$, the habit of the crystals being tabular through $\infty\breve{P}\infty$, in combination, however, with brachyprisms and brachydomes. The structure of the crystals is more in harmony with a polysynthetical twin-formation of a monosymmetrical or asymmetrical species.

Hessite.—The specimens examined came from Rezbanya, and the author concludes that this mineral crystallises in the regular system, the forms observed being $0.\infty0\infty.\infty0.20$, and $\infty03$, the latter form occurring on a pyramidal distorted crystal. Hessite, Ag_2Te, is therefore isomorphous with argentite.

Tellursilberblende, a new species.—Monosymmetrical, 50 faces being observed on the crystal examined. Colour lead-grey, with a characteristic adamantine lustre. Formula corresponding with the chemical composition $= Ag_4Te$. Schrauf proposes calling this new mineral "stützite." C. A. B.

Sulphide of Silver from Andreasberg. By A. Streng (*Jahrb. f. Min.*, 1878, 785—799).—In 1875 the author described as magnetic iron-pyrites a mineral which he found attached to pyrargyrite, from Andreasberg, and which had been sent to him as marcasite. The forms exhibited by the crystals were apparently $P.\infty P.\infty P2$, and Streng concluded that the mineral was magnetic iron-pyrites, and not marcasite (1) because the mean of some measurements of the angle $\infty P:\infty P2. = 150°$; (2) it was slightly magnetic; (3) it evolved a little sulphuretted hydrogen on being treated with hydrochloric acid; (4) because it coincided perfectly with a crystal from Andreasberg, belonging to the Giessen University Museum, which was considered to be a typical magnetic iron-pyrites crystal. The author has examined the specimens further, and finds that the crystals under discussion are neither marcasite nor magnetic iron-pyrites, but that they belong to the *silver ores*, being led to this conclusion from reading Weisbach's paper on the sulphurets of silver (*Jahrb. f. Min.*, 1877, 908); Tschermak's paper (*Sitzb. d. Wiener. Akad.*, 1866, **54**); and Schrauf's paper (*ibid.*, **64**, 192). The typical crystal exhibited the following characteristics:—It was 2 mm. long and broad, and apparently a combination of the predominating hexagonal prism of the first order with the prism of the second order, and a very obtuse, horizontally striated pyramid. No striation was observed on the prismatic faces, but a closer examination showed that each face of $\infty P2$ was divided vertically by a line, but in such a manner that the two halves were almost in the same plane. The terminal edges of the pyramid were indented,

and this occurrence was evidently intimately connected with the salient angle on $\infty P2$, whence it was highly probable that the crystal was either a rhombic twin or trilling. The crystals from Andreasberg (described in 1875) exhibited similar characteristics, the pyramidal faces being somewhat convex, owing to their being strongly horizontally striated; they are homogeneous internally, the colour being light brass-yellow, but their outer surface often exhibits a liver-brown, pinchbeck-brown, steel-blue, dark green, or variegated tarnish. Strong metallic lustre. H. = 3·5 to 4. Sp. gr. = 4·18 at 19° C. Cleavage not distinct; fracture uneven, streak dark blackish-green to dark greyish-green. Slightly brittle and magnetic. A chemical examination of the crystals proved them to contain (in addition to sulphur) considerable amounts of silver, whence it is evident that they are not magnetic iron pyrites crystals, but are undoubtedly sulphide of silver. The author measured carefully eight crystals, and found that the interfacial angles in the vertical zone varied from 149° 31′ to 150° 30′, and on referring these angles to the axial ratio obtained by Schrauf, in the case of argentopyrites, viz.:—a = brachyaxis : b = macroaxis : c = vertical axis = 0·58124 : 1 : 0·27487, he concluded it was highly probable that a prism $\infty\breve{P}3$, hitherto unknown to silver-sulphide, was combined with ∞P, the calculated angle for this combination being 150° 0′. The angle might also arise in the combination of $\infty\breve{P}3$ with $\infty\breve{P}\infty$, the calculated angle for this combination being 150° 10′. From the author's observations it appears highly probable that the crystals are rhombic, and not hexagonal, being penetration trillings according to the law, the twin-plane a face of ∞P, the combination observed being $\infty\breve{P}\infty.\infty\breve{P}3.2\breve{P}\infty$; the latter form occurring in oscillatory combination, either with 0P, or with an extremely obtuse brachydome $m\breve{P}\infty$. The chemical composition of the crystals was as follows, viz.:

Ag.	Cu.	Fe.	S.
32·89	0·19	35·89	30·71 = 99·74

the formula deduced from this being $Ag_2S.Fe_4S_5$. Streng then compares the above analysis with those of—1. Sternbergite, from Marienberg (Rammelsberg). 2. Sternbergite, from Marienberg (Zippe). 3. Argyropyrites, from Marienberg (Winkler). 4. Frieseite, from Joachimsthal (Fries). 5. Argentopyrites, from Joachimsthal (Waldershausen).

	Ag.	Cu.	Fe.	S.
1. ..	35·27	—	35·97	29·10 = 100·34
2. ..	32·0	—	36·0	30·0 = 99·2
3. ..	29·75	—	36·28	32·81 = 98·84
4. ..	29·1	—	33·0	37·4 = 99·50
5. ..	26·5	—	39·3	34·2 = 100·00

Leaving out No. 4, the general formula for the above-mentioned minerals is $Ag_2S + pFe_nS_n + 1$, and as their crystal forms agree very closely, it may be inferred that they are isomorphous. They differ however somewhat in their physical properties, sternbergite, frieseite,

and argyropyrites having a hardness of 1·5, a distinct basal cleavage and flexibility, whilst argentopyrites has a hardness of 3·5 to 4, no cleavage, and has no flexibility. All the above-mentioned minerals are mixtures of Ag_2S, with varying amounts of a differently constituted sulphide of iron. The author points out the parallelism existing between the change in composition of the iron sulphide in the silver sulphide, and the change in the amount of sulphur in magnetic iron-pyrites, and asks the question, "Can the sulphide of silver in question be considered as an isomorphous mixture of acanthite, with magnetic iron-pyrites?"

Streng considers it probable that magnetic iron pyrites crystallises in the rhombic system, and as the type is hexagonal, like that of the sulphide of silver above described, he states that this may be accounted for by a trilling formation. The hexagonal forms generally observed on magnetic iron-pyrites are as follows, viz.:—

$$\tfrac{1}{2}P.P.2P.\tfrac{1}{2}P2.P2.\infty P.\infty P2.0P.$$

Taking Schrauf's rhombic axial ratio in sulphide of silver as the standard, the above hexagonal forms resolve themselves into the following forms, viz.:—$\frac{1}{2}P = \frac{1}{6}^{1}P.$, $P = \frac{1}{3}^{1}P.$, $2P. = \frac{2}{3}^{2}P.$, $\frac{1}{2}P2 = \frac{1}{6}^{1}\bar{P}\infty.$, $P2. = \frac{1}{3}^{1}\bar{P}\infty.$, $\infty P2 = \infty\breve{P}3$. The author gives a table of forms in which all the above-mentioned minerals crystallise, and compares the rhombic forms (obtained by taking Schrauf's axial ratio of sulphide of silver as the standard) with the supposed hexagonal forms of magnetic iron pyrites, and the hitherto accepted rhombic forms of copper-glance (redruthite), and concludes by stating that it is probable that magnetic iron-pyrites, sulphide of silver (silber-kies), and copper-glance (with acanthite) are isomorphous. C. A. B.

Crystallographical and Chemical Examination of some Arsenical Pyrites (Mispickel). By A. Arzruni (*Jahrb. f. Min.*, 1878, 860—862).—Crystals of mispickel from the Binnenthal dolomite, sometimes attaining a size of 4 mm., are developed in the direction of the brachyaxis, exhibiting the following forms in combination, viz., $\infty P.P\breve{\infty}.\frac{1}{2}P\breve{\infty}$, and occur twinned according to both laws. Mispickel from Hohenstein in Saxony exhibits the following forms in combination, viz., $P\bar{\infty}.\infty P$, very smooth and predominating, the crystals being developed in the direction of the macroaxis,

$$P\breve{\infty} . \tfrac{1}{3}P\breve{\infty} . \tfrac{1}{4}P\breve{\infty} . 0P,$$

these faces being quite secondary, and strongly striated parallel to the brachyaxis. Freiberg mispickel occurs in two types, the first being rich in faces, $\infty P.P\breve{\infty}.\frac{1}{2}P\breve{\infty}$ predominating, whilst $P\breve{2}$ occurs, occupying a secondary position; but no twins were observed with this type. Crystals of the second type are not rich in faces, the only forms observed being ∞P, $\frac{1}{3}P\breve{\infty}$; but twins were the rule according to the law the twin-plane a face of $P\bar{\infty}$. The author did not observe the dome $\frac{1}{4}P\breve{\infty}$ on Freiberg mispickel, in contradiction to the statements of other authors, in fact, he only observed it on mispickel crystals from Hohenstein. Mispickel crystals from Ehrenfriedersdorf, occur also in two types, the first being simple, "short-prismatic," with $\infty P.P\bar{\infty}$ in com-

bination, whilst the second type includes the so-called *plinian* of Breithaupt, which Arzruni and G. Rose agree in stating is nothing more than a distorted mispickel. The somewhat rare mispickel crystals from Reichenstein are prismatic in habit, the following forms being observed, viz., ∞P.P$\breve{\infty}$.$\frac{1}{2}$P$\breve{\infty}$. The crystals found at Mitterberg, near Mühlbach, in Salzburg, are pyramidal in habit, through P$\breve{\infty}$.$\frac{1}{2}$P$\breve{\infty}$, whilst ∞P. is only very secondary. The author observed a new obtuse brachydome $\frac{1}{16}$P$\breve{\infty}$ on the crystals from Joachimsthal (described by Gamper (*Jahrb. f. Min.*, 1877, 204), which are tabular in habit, through 0P. and some brachydomes. Arzruni's conclusions from his research are briefly as follows:—1. The chemical composition of mispickel changes with the locality, neither of the formulæ $FeAs_2 + FeS_2$, or $mFeAs_2 + nFeS_2$ expressing accurately its chemical composition; were the latter formula correct it would be a direct proof of the isomorphism of $FeAs_2$ and FeS_2. 2. The amount of iron in all mispickel is very constant, the maximum difference being only 0·32 per cent. (Reichenstein and Freiberg, second type), whilst there is an intimate connection between the regular increase of the percentage of sulphur and the growth of the prismatic angle. C. A. B.

Mallardite, a new Natural Manganese Sulphate, and Luckite, a new variety of Iron Sulphate. By A. Carnot (*Compt. rend.*, **88**, 1268—1270).—*Mallardite* is found in small fibrous monoclinic crystals, which at first are colourless and transparent, but effloresce rapidly on exposure to air. The crystals have the composition $MnSO_4.7H_2O$. On efflorescence they lose $2H_2O$.

Luckite occurs in small, distorted crystals, probably belonging to the monoclinic system. They have a slight blue tinge, and have the composition $SO_4(MnFe) + 7H_2O$, the ratio of manganese to iron being about 1 to 10. This mineral is therefore intermediate between melanterite and mallardite, from both of which it is distinguished by the fact that it does not alter on exposure to the air.

Mallardite and luckite were found at the Lucky Boy silver mine, near Butterfield Cañon, Utah, U.S. C. H. B.

Growth-phenomena on Quartz Crystals from Krummendorf, near Strehlen. By E. Schumacher (*Jahrb. f. Min.*, 1878, 822—825).—The author observed some peculiar quartz crystals, which exhibited apparently the basal terminal plane in combination with ∞R. + R. −R, and he describes also a quartz crystal belonging to the Breslau collection, which, in addition to the above-mentioned forms, has a peculiar step-like growth, but the reasons given by him for these unusual occurrences cannot be clearly understood without reference to the drawings given in his paper. Schumacher is of opinion that the supposed basal plane on these crystals is most probably an abnormal growth, caused by the collision of two crystals with each other at right angles during growth. C. A. B.

Cacochlor, from Rengersdorf, near Görlitz. By A. Weisbach (*Jahrb. f. Min.*, 1878, 846—849).—The author examined some specimens of this mineral, sent to him by Prof. Geinitz, and observed that

the polyhedral impressions referred to by Geinitz were formed by four faces, of which each pair intersecting in an edge was alike. The crystals were most likely rhombic, and Weisbach concluded from his measurements, and the physical characteristics of the pyramidal faces, that they had been originally lievrite crystal; consequently the cacochlor in this instance was a pseudomorph after lievrite, as cacochlor is doubtless an amorphous and porous mineral. The only analysis of this mineral extant being one by Klaproth, published in 1797, a new analysis of it was made by Winkler. The chemical composition, as given by Klaproth and by Winkler, is as follows, viz.:

	MnO_2 (containing CoO).	CuO.	SiO_2.	Al_2O_3.	H_2O.
Klaproth	35·4	0·2	24·8	20·4	17·0 = 97·8

	MnO.	O.	CoO.NiO.	CuO.	Fe_2O_3.	Al_2O_3.
Winkler	43·46	9·20	2·55	0·53	0·83	14·33

BaO.	Li_2O.	K_2O.	SiO_3.	H_2O.
0·82	0·91	1·26	13·78	12·33 = 100·00

From this last analysis it is evident that cacochlor is nearly related to the asbolan of Saalfeld and the lithiophorite from the "Gott segne beständig" mine below Eibenstock. C. A. B.

Idocrase in the Limestone-strata of Deutsch-Tschammendorf. By E. Schumacher (*Jahrb. f. Min.*, 1878, 817—821).—The limestone of this locality has a light green colour and a considerable degree of hardness, owing to the presence of innumerable enclosed microscopical diopside grains. Titanite occurs also, as a constituent of the rock, in numerous microscopical grains, accompanied by microscopical quartz grains. These enclosures sometimes increase so much in number that eventually the rock contains only a trace of limestone, and to all appearance becomes a quartzite. The limestone occurs in distinct strata, and is penetrated by dark-brown bands running parallel with the stratification. Some of these bands consist of scaly brown mica, whilst others are formed out of brown-red or liver-brown idocrase in flattened, granular, or columnar masses. The idocrase masses often enclose vertically striated crystals, exhibiting the forms ∞P. $\infty P\infty$ and ∞Pn, the terminals being nearly always broken off; the author, however, once obtained a well-defined crystal exhibiting the following forms in combination, viz.: $\infty P.0P.\infty P\infty.P$. A careful chemical examination showed that the idocrase had the following composition:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	FeO.	CaO.	MgO.	H_2O.
37·80	1·77	16·28	1·56	0·94	3·11	34·76	2·42	2·29 = 100·93

This analysis agrees tolerably well with Rammelsberg's analysis of idocrase from Monzoni (*Min. Chim.*, 602). No microscopical titanite enclosures were observed by the author in the idocrase crystals, and as 1·77 per cent. of titanic acid would represent 4·3 per cent. of titanite, he concludes that the titanic acid replaces an equivalent amount of silica in the idocrase. C. A. B.

Granular Plagioclase in the Limestone-strata of Geppersdorf, near Strehlen, Silesia. By E. Schumacher (*Jahrb. f. Min.*, 1878, 814—817).—The limestone at Geppersdorf is occasionally covered with wedge-shaped granite masses, which probably were originally portions of a granite fault touching the limestone on the west side, whilst on the eastern side the limestone is covered by quartzite, and becomes slaty and fibrous in structure, particularly in the upper layers. The fibrous structure is caused by alternating plates of blue-grey limestone, and layers consisting of (1) granular plagioclase and lenticular flattened quartz grains; (2) asbestos attached to aggregates of white or greenish columnar diopside, mixed with grey or greenish fibrous tremolite; (3) garnet-rock, consisting of brown-red garnet and green epidote; (4) quartz and semiopal. The last-mentioned layer is a rare occurrence. The layers generally run parallel one under the other, but they occur also in a very irregular and undulating manner. The felspar is either snow-white in colour, fine-grained and somewhat soft, or else perfectly massive, greyish-white and rather hard. The fine-grained variety on being examined under the microscope, proved to be almost pure, no grains of quartz being present, and only a few isolated grains of colourless diopside, whilst the massive variety contained more diopside than the granular, but no quartz. Orthoclase was probably intermixed with the plagioclase, but its presence could not be ascertained with certainty, owing to the impossibility of preparing sufficiently thin sections from such brittle material. An analysis of the snow-white granular variety furnished the following results, viz.:—

SiO_2.	Al_2O_3 (containing trace of Fe_2O_3).	CaO.	MgO.	Na_2O.	H_2O.
57·87	26·32	9·22	0·92	5·39	0·28 = 100·00

According to Tschermak's law, the above analysis shows that the mineral in question is an isomorphous mixture of 2 molecules of anorthite, with 1 molecule of albite, and the formula therefore = $2\left(\begin{matrix}CaSi_2O_8\\Na_2Si_6O_{16}\end{matrix}\right)$. The amount of silica found by analysis is somewhat higher than that required by the above formula. C. A. B.

Basalts of the Auckland Islands. By Max Hartmann (*Jahrb. f. Min.*, 1878, 825—830).—The specimens of basalt were obtained when the German Expedition visited the islands for the purpose of observing the transit of Venus, in 1874. All the islands are of plutonic origin, being built up of trachyte, which is penetrated here and there by eruptions of basalt. The specimens examined by the author came from the Hooker Hills, and are pebble-like in appearance, some being perfectly smooth, whilst others have the slag-like blebby appearance of lava, and exhibit on their rough surfaces brown-red olivine crystals 2 mm. in length, on which the forms $\infty P\infty$. $\infty\breve{P}\infty$. $\bar{P}\infty$. can be distinctly recognised. Generally speaking, the Auckland basalts are identical with the different types of European basalts, but they are somewhat more doleritic in character. A microscopical examination proved them to be plagioclase-basalts. The

plagioclase-dolerites consist of predominating augite, plagioclase and olivine, the ground-mass being almost completely displaced. The augite crystals sometimes attain a length of from 4 to 5 mm., and a breadth of from 2 to 3 mm. In thin sections these crystals appear almost colourless, rose-coloured, or light-brown, often with a distinct zonal structure, and commonly twinned parallel to $\infty\breve{P}\infty$. The enclosures of the augite crystals are irregular in form, and consist mostly of glass-substance, but magnetite is observed occasionally, together with very rare biotite laminæ. On some augite sections it was observed that some portions of the augite mass were optically different from the others. The olivine crystals are mostly colourless and fresh, a brown or green reticulated product of decomposition being generally observed on the outer edges only. Sections of the olivine crystals made parallel to 0P. generally exhibit some enclosed ground-mass in their interiors. The plagioclase crystals are 6 mm. long and $2\frac{1}{2}$ mm. broad, mostly colourless, fresh, and exhibit a distinct polysynthetical twin-formation according to two laws, the first being "the twin-axis the normal to M.($\infty\breve{P}\infty$.)," the second "the twin-axis the macro-axis," whilst from the optical properties observed the author concludes that the plagioclase resembles labradorite. The enclosures in the plagioclase are gas-pores, augite-microlites, magnetite grains, and irregularly formed glass-substance. The ground-mass in the dolerites consists of very numerous light, long, plagioclase crystals, exhibiting distinct twin-striation, and generally entirely free from enclosures, mixed with brownish augites, augite-microlites, and a great quantity of evenly distributed grains of magnetite. Larger masses of magnetite occur either rounded off or else exhibiting distinct signs of crystallisation. Apatite occurs but sparingly, and then in long colourless needles. No interpolations of glass-substance could be detected in the ground-mass. Zeolitic formations are of common occurrence in round hollow spaces, and there were indications of the presence of nepheline. The ground-mass of the plagioclase-anamesite and plagioclase-basaltite is very nearly the same as that of the dolerite, but the acicular apatite was present in much greater quantity, and the olivine occurred in small grains. The anamesites contain only very small felspar and olivine crystals, the latter enclosing ground-mass. The true basalts contain olivine and plagioclase disseminated porphyritically throughout, the former mineral being more or less decomposed into ferric oxide and enclosing picotite, fluid, glass-pores and gas-pores. The plagioclase and augite crystals were characterised by numerous enclosures of the same character as those observed in the plagioclase and augite referred to above. The hollow spaces in the anamesites and basaltites are generally filled with zeolitic formations. Sphärosiderite occurs very commonly in round, dark-brown masses. Nepheline was only observed in two sections of true basalt. The author concludes by stating that the characteristic feature of the Auckland Island basalts so far examined is the almost complete absence of glassy substance. C. A. B.

Cinders and Lava from Etna. By A. Cossa (*Compt. rend.*, **88**, 1358—1359).—The cinder and lava thrown out during the recent

eruptions of Etna were obtained, the former from Reggio de Calabre, the latter from the neighbourhood of Giarre.

The cinder is of a grey colour, and contains about 12 per cent. of magnetite; it is formed of crystals of triclinic felspar, augite, magnetite, and a large quantity of splinters of different-coloured glass. The felspar is colourless, and contains a great number of elliptical and irregular cavities filled with glass. In this glass, which is for the most part coloured grey, but sometimes of a red or green colour, empty bubbles are found, and some microliths of augite and apatite. The cinder contains 18 per cent. of matters soluble in hydrochloric acid, and consists of silica, titanic anhydride, phosphoric anhydride, ferrous and ferric oxide, manganous oxide, lime, magnesia, soda and potash. Its spectrum shows the lines of strontium and lithium.

The lava is composed of triclinic felspar, disseminated through a microcrystalline magma of augite, magnetite, and a small quantity of vitreous matter. L. T. O'S.

Report on the Researches of S. Meunier relative to Meteoric Nickeliferous Iron and the Native Carburetted Iron of Greenland. By Fremy, H. St. Claire Deville, Des Cloizeaux, Debray, and Daubrée (*Compt. rend.*, **89**, 215—219).—This report contains a short summary of Meunier's papers (*Compt. rend.*, **87**, 855, and **88**, 794 and 924). He regards the native iron of Greenland as having been brought up by the basalt which contains it, from beds lying at a very great depth. C. H. B.

Note.—J. Lawrence Smith (this vol., p. 892) has recently brought forward evidence to show that the native iron of Greenland has been formed by the reduction of the basalt by the carbonaceous matter through which it was injected.—C. H. B.

Amount of Nitric Acid in the Waters of the Nile. By D'Abbadie (*Compt. rend.*, **88**, 1117—1119).—Boussingault has given 0·004 gram of nitric acid, or 0·0075 of potassium nitrate per litre, as the amount contained in the Nile waters in 1859, during the rise, compared with 0·002 in those of the Rhine and of the Seine. From this it is calculated that the Nile every day carries into the sea more than a million kilos. of saltpetre. R. R.

Analysis of the Water of St. Dunstan's Well, Melrose. By W. Johnstone (*Chem. News*, **39**, 259).—This is a strongly ferruginous, saline, carbonated water. An analysis of it was made in 1870, by J. Dewar (*Chem. News*, **24**, 171), but the water has since considerably changed. The spring was discovered by Mr. J. Turnbull, in 1870, in sinking a shaft for ordinary spring water.

The water is clear, but of a yellowish colour; on exposure to the air it deposits iron as a ferric mangano-manganic oxide; it has a strong "powdery" odour, and a decidedly inky taste. It is always very cold (about 50° F. when the temperature of the air was 62° F.), and its sp. gr. is 1001—1356.

The following is the analysis of the water given in parts per million:—Cl, 378·243; Br, 0·305; I, 0·788; SO_3, 74·258; CO_2 (total), 682·183; SiO_2, 35·286; FeO, 328·680; $CaCO_3$ and $SrCO_3$, 103·842; MgO (total), 56·216; $CaCO_3$, precipitated as carbonate on boiling, 28·544; BaO, 2·917; SrO, 0·886; MnO, 0·785; P_2O_5, 20·085; Al_2O_3, 6·582; Li_2O, 0·282; K_2O, 6·258; Na_2O, 343·063; NH_3, 18·652. Total, fixed constituents, 1390·000.

The author examined the residue from 30 gallons of the water by the spectroscope for cæsium, rubidium, and thallium, but failed to find them.

Gases dissolved in 1 litre of the water and expelled by ebullition in a vacuum, measured, at 59° F. and 760 mm. barometer, CO_2, 101·434 c.c.; O, 6·793; N, 31·250. Total, 139·477.

In addition to the above constituents, the author found fluorine and butyric, phosphoric, crenic, and apocrenic acids. W. T.

Water from the River Dart. By T. L. Phipson (*Chem. News*, **40**, 54).—In some notes recently published, the author alluded to the importance of the indication furnished by phosphoric acid in the analysis of potable waters, and to an examination of the specimen of water from the River Dart, taken at a portion of its course, where it was found to be injurious to fish, and killed large numbers of trout. This water was somewhat turbid, and showed a slight deposit of organic matter. It was neutral to test-paper, and gave grains per gallon: total residue, 52·50; nitrogenous organic matter, 17·5 (burning with a bad odour); phosphoric acid, 3·25; and mineral matters, 31·75 (chiefly silica, calcium sulphate, and alkaline salts). The strata through which this water flows is the chalk of Kent. The presence of so much organic matter and that of phosphoric acid to so large an amount, points either to sewage contamination or to refuse from chemical works finding its way into the river near the spot, where this sample of water was taken. The former suggestion appears most probable. D. B.

Analysis of the Waters of Lake Thirlmere and the River Vyrnyw. By C. Estcourt (*Chem. News*, **40**, 39).—The following are the results of the author's analyses, together with those of Messrs. Grimshaw, of Thirlmere. The author's samples were taken in the winter of 1877, those of Grimshaw in August, 1878:—

Per gallon.	Thirlmere water, unfiltered.				Vyrnyw filtered. Estcourt.
	Estcourt. Head of lake.	Grimshaw. Upper.	Estcourt Outlet.	Grimshaw. Lower.	
Total solid matter	2·25	2·20	3·10	3·15	5·16
Mineral do.	1·10	1·56	1·15	1·40	1·46
Loss on ignition	1·15	0·70	1·95	1·75	3·70
Hardness (all permanent)	2·25	1·00	1·50	1·00	2·75
Cl	0·58	0·42	0·44	0·70	0·41
Ureal ammonia	—	—	0·0009	0·0021	0·0154
Albuminoid do.	—	—	0·0042	0·0042	0·0056
Colour	None	—	None	—	Pale yellow

It will be perceived that all analyses of Thirlmere water give results within limits of extreme purity. In the Vyrnyw water the amount of organic matter which it contains is indicated readily by its peaty colour. D. B.

Organic Chemistry.

Action of Oxidising Agents on the Olefines. By O. and F. Zeidler (*Liebig's Annalen*, **197**, 243—256).—The authors have experimented with the following agents:—(*a*) an aqueous solution of potassium permanganate; (*b*) a solution of potassium permanganate acidified with sulphuric acid; (*c*) an alkaline solution of potassium permanganate; (*d*) a solution of chromic acid; and (*e*) a mixture of potassium dichromate and sulphuric acid. In each case 2—3 litres of the gaseous olefine were used, and the proportion of oxidising agent taken so as to represent 4 mols. of oxygen to 1 mol. of olefine.

Ethylene yielded the following results:—With (*a*) formic, acetic, and oxalic acids; (*b*) carbonic, formic, acetic, and oxalic acids (traces); (*c*) carbonic, formic, acetic, and oxalic acids; (*d*) no action at the ordinary temperature, but at 100° carbonic acid, and small quantities of formic, acetic, and oxalic acids are formed; (*e*) the same as (*d*). These results differ somewhat from those obtained by Truchot (*Annalen*, **141**, 108); Berthelot (*Compt. rend.*, **64**, 35; *Annalen Suppl.*, **5**, 95; *Compt. rend.*, **68**, 333; *Annalen*, **150**, 373; *Ann. Chim. Phys.*, 1875 [5], **6**, 449); and by Chapman and Thorp (*Annalen*, **142**, 182).

Propylene yielded (*a*) carbonic, oxalic, and acetic acids, and traces of an acid perhaps succinic or malonic acid; (*b*) carbonic, acetic, oxalic acids, a little formic acid, and traces of an acid which may be either malonic or glycollic acid; traces of acetone; (*c*) carbonic, acetic, oxalic acids, traces of formic acid, and probably malonic acid, also a

small quantity of acetone; (*d*) small quantities of carbonic acid, but large quantities of formic and acetic acids, and only a trace of oxalic acid; (*e*) the same result as (*d*).

Isobutylene, $(CH_3)_2C : CH_2$, prepared from fermentation butyl iodide, was used, and yielded the following results:—(*a*) carbonic acid, small quantities of acetic and formic acids, the chief product was oxalic acid; (*b*) carbonic, formic, acetic, and oxalic acids; (*c*) carbonic, small quantity of formic, acetic, and oxalic acids; (*d*) no action in the cold, only at temperatures of steam-bath, yielding carbonic, formic, acetic, and oxalic acids, also acetone; (*e*) the same as (*d*), the action is, however, more energetic. Isobutylene does not in any case yield succinic acid.

One of the authors (*Annalen*, **186**, 247) obtained by the oxidation of amylene, b. p. 35°, butyric and succinic acids. Since then, Wischnegradsky (*Annalen*, **190**, 328) has shown that this olefine consists of two isomerides, one of which is trimethylethylene, and the other either propylethylene or ethylmethylethylene. The latter (b. p. 35—37°), prepared from ordinary amylene by means of its insolubility in sulphuric acid, yields on oxidation with an alkaline solution of potassium permanganate, succinic and oxalic acids, also formic and butyric acids, and traces of carbonic acid. These results show the constitution of this amylene to be $CH_3.CH_2.CH_2.CH : CH_2$, *i.e.*, propyletbylene, and not ethylmethylethylene.

In conclusion, the authors point out that the difference in action between the oxidising agents is a quantitative and not a qualitative one; further, that the olefines are attacked at the point of double union. The resulting monobasic acids are, as shown by P. de St. Gilles (*Compt. rend.*, **46**, 811) and Berthelot (*Annalen Suppl.*, **5**, 95, and **6**, 181), further oxidised to bibasic acids. The formation of acetic acid from ethylene, and of malonic acid from propylene, may be explained by supposing the addition of water as H and OH to take place; for instance, in the case of ethylene, a primary alcohol would be formed, and the molecule not broken up. In the case of propylene, the addition may take place so as to form the primary or secondary alcohol, thus explaining the formation of malonic acid and acetone:

$$CH_3.CH : CH_2 + H.OH = CH_3.CH_2.CH_2(OH), \text{ or}$$
$$CH_3.CH : CH_2 + HO.H = CH_3.CH(OH).CH_3.$$

P. P. B.

The Two Isomeric Dibromopropanes. By E. Erlenmeyer (*Liebig's Annalen*, **197**, 169—185).—This is an account of an investigation of the conditions under which propylene bromide, $CH_3.CHBr.CH_2Br$, and trimethylene bromide, $CH_2Br.CH_2.CH_2Br$, are formed. Reboul's method (*Compt. rend.*, **74**, 613, and **76**, 1270) of saturating allyl alcohol with hydrobromic acid gas, the author finds yields chiefly allyl bromide. In conjunction with Kayser (Inaug. Dissert., *München*, 1875), the author has found that when hydrobromic acid gas reacts on the vapour of allyl bromide, trimethylene bromide is the chief product. Julie Lermontoff (*Annalen*, **182**, 358), however, has found this method to give but a poor yield. She proposes to prepare trimethylene bromide by saturating allyl bromide at −10° to 15°

with hydrobromic acid, and heating the product in sealed tubes at 166—170° for 24 hours. The author, in conjunction with F. Fischer, has repeated these experiments, and finds that the two bromides are formed in this way. If, however, hydrobromic acid gas be passed into allyl bromide at 20° until it is saturated and the product distilled in a water-bath, a residue is obtained consisting chiefly of trimethylene bromide; and when the temperature falls as low as 12°, some propylene bromide is formed. The conditions for the formation of these bodies are further illustrated by the experiments in which allyl bromide saturated with hydrobromic acid gas at 16—19° was exposed in glass vessels, one at 10° to diffused daylight, another to direct sunlight, and the third in the dark to a temperature of 35—40°. The last two yielded trimethylene bromide only, the former 81 per cent., the latter almost 100 per cent., whilst the first yielded only small quantities of the two bromides. From these experiments the author draws the following conclusions:—(1) the most favourable conditions for the formation of trimethylene bromide are that the dry hydrobromic acid gas should be in large excess of the allyl bromide until the reaction is ended and the temperature should be maintained at 30—40°; (2) the more diluted the hydrobromic acid becomes, either by water or by trimethylene bromide, the larger is the quantity of propylene dibromide formed. When the required dilution has been produced by the formation of trimethylene bromide, the remaining hydrobromic acid unites with allyl bromide to form propylene bromide, this reaction taking place more quickly at high than at low temperatures; (3) the formation of trimethylene bromide takes place first at temperatures from 0—30°, and, in case of sufficiently concentrated solutions, even at temperatures above 100°. The formation of propylene bromide commences in dilute hydrobromic acid solutions at low rather than at high temperatures. The methods for preparing trimethylene bromide proposed by Reboul (*Ann. Chim. Phys.* [5], **14**, 470) and by Bogomolez (*Ber.*, **11**, 1287), yield mixtures of the two bromides, the last mentioned yielding chiefly propylene bromide.

P. P. B.

Direct Combination of Cyanogen with Hydrogen and the Metals. By Berthelot (*Compt. rend.*, **89**, 63—68).—The consideration of thermal data showed that cyanogen, like chlorine, should combine directly with hydrogen. The production of hydrocyanic acid by the action of electric sparks on a mixture of cyanogen and hydrogen is possibly the result of a secondary action, and not a direct combination, acetylene and free nitrogen being first produced; and then under the influence of the sparks combining to form hydrocyanic acid. The author found that when equal volumes of hydrogen and cyanogen were passed slowly through a glass tube heated to 500—550°, only 4—6 per cent. of the mixture was converted into hydrocyanic acid; but when the two gases were heated in a sealed tube to 500—550° for several hours, 29 per cent. of the cyanogen was converted into paracyanogen, an equivalent amount of hydrogen remained free, and the remainder of the gases combined, forming hydrocyanic acid.

Attempts were made to obtain cyanides by the direct union of cyanogen with metals. When the gas was heated in sealed tubes at

300° with Zn, Cd, and Fe, cyanides of the metals were formed, together with some paracyanogen, but no free nitrogen. The amount of cyanogen absorbed depended on the area of metallic surface exposed. Zinc was attacked at the ordinary temperature after some days; at 100°, after a few hours. Cadmium was not attacked in the cold, and only slightly at 100°. Iron was not acted on at 100°. Copper and lead gave no cyanide at 100° or 300°, but at 500—550°, small quantities were formed, together with carbonaceous matter and free nitrogen. The same was the case with iron at 550°. Silver and mercury did not combine with the cyanogen at any temperature. The author regards hydrocyanic acid as forming a connecting link between the formic and ethylic series, since under certain circumstances it is converted into formic acid and into methane, under others into oxalic acid and also into ethane. The direct combination of cyanogen with hydrogen and the metals strengthens the analogy already existing between that radicle and the halogens. C. H. B.

Reactions of Cyanamide. By G. Praetorious-Seidler (*J. pr. Chem.* [2], **19**, 399—400).—Erlenmeyer having effected the synthesis of guanidine hydrcchloride from cyanamide and ammonium chloride, the author inferred the probable formation of oxyguanidine by the reaction of cyanamide and hydroxylamine hydrochloride. The attempt to realise this reaction was successful in so far as a crystalline platinochloride, having the composition $[CN_3H_5O.HCl]_2PtCl_4$, was obtained, but oxyguanidine itself could not be isolated. Cyanamide and salicylic acid, in solution in absolute alcohol, react together with formation of urea and ethyl salicylate—apparently according to the equation: $2.C_6H_4(OH)COOH + CN.NH_2 + 2EtOH = CO.N_2H_4 + 2.C_6H_4(OH)COOEt + H_2O$. Cyanamide and lactic acid also react in presence of alcohol, with formation of urea, but no ethyl derivatives could in this case be detected. The action of cyanamide on phenol and thiacetic acid, gives rise to well crystallised products, which are under investigation. C. F. C.

Action of Bleaching Powder on Ethyl Alcohol. By R. Schmitt and Goldberg (*J. pr. Chem.* [2], **19**, 393—396).—A mixture of absolute alcohol (1 part) and bleaching powder (4—5 parts) becomes spontaneously heated after the lapse of 7—10 minutes, when aldehyde, acetal derivatives, and unaltered alcohol distil over, together with a greenish-yellow oil, which is rapidly decomposed under the influence of light, with evolution of hydrochloric and hypochlorous acids. The authors have not yet succeeded in isolating this body, but from its mode of formation and decomposition they regard it as ethyl hypochlorite. After the decomposition of this oil has taken place, the distillate contains 20 per cent. of its weight of a heavy oil insoluble in water. This when submitted to fractional distillation yields monochloracetal, dichloracetal, and a compound with constant boiling point (77—78°), probably a chlorinated ethyl-methyl ether. The portions boiling below 77° are chlorinated products, exhibiting increasing percentage of chlorine with decreasing boiling temperature.

Monochloracetal treated with bleaching powder also enters into

spontaneous distillation in consequence of the heat evolved in the reaction.

The distillate yields dichloracetal and a product boiling at 70—80°. The further investigation of these reactions is in progress.

C. F. C.

Behaviour of Gums and Carbohydrates towards Chromates under the Influence of Light. By J. M. Eder (*J. pr. Chem.* [2], **19**, 294—301).—Potassium or ammonium dichromate forms with gelatin, gums, sugar, dextrin, and albumin, a coagulum which is altered by exposure to light. Many qualitative reactions of the coagulums, both before and after exposure to light, are detailed.

The coagulums generally become insoluble in water after being exposed to light: they undergo this change more rapidly when moist than when dry. In the case of gelatin, the chromate is reduced, with formation of chromium chromate, and the insoluble coagulum consists of this body united with unaltered gelatin. The main product of oxidation of the gelatin is formic acid, which goes into solution on treatment with water. Sugar forms with chromates a coagulum, which is altered by exposure to light, with production of formic acid (no saccharic or oxalic acid is produced). The coagulum does not become insoluble in water.

The coagulum of gum arabic (and gum tragacanth) is insoluble in water after exposure to light, and contains chromic oxide and metagummic acid. The coagulum of albumin is very sensitive to light: after exposure it becomes insoluble in water, and seems to contain some oxidised derivative of albumin, together with chromic oxide. M. M. P. M.

Action of Heat on Sugar and Sugar Solutions. By Motten (*Bied. Centr.*, **8**, 55—56).—A temperature of 100° has a very slight action in decreasing the rotatory power of a solution of sugar. A solution of sugar gave 64° instead of 65·7° after 15 hours heating at 100°.

The slight change which sugar undergoes when heated for some hours at 100° is due to a trace of moisture; when it is heated for 360 hours in the presence of one-tenth of its weight of water, nearly 44 per cent. of the sugar had become altered. A. J. C.

Conversion of Hydrocellulose into Pyroxylin. By A. Girard (*Compt. rend.*, **89**, 170—173).—When acted on by a mixture of nitric and sulphuric acids, hydrocellulose undergoes nitrification to the same degree as cellulose, and is converted into the same products, which are, however, very friable. The hydrocellulose is more easily acted on when in the fibrous condition, and is probably dehydrated before nitrification. The products thus obtained behave like ordinary pyroxylin, but when they are reduced to impalpable powder their properties are analogous to those of dynamite. Their friability renders them very soluble in mixtures of alcohol and ether, and these solutions appear to possess peculiar photographic properties. C. H. B.

Composition of Beetroot Gum. By N. Bunge (*Bied. Centr.*, 1879, 56).—In continuation of the investigations of Scheibler, Feltz, and Borschtschoff (*ibid.*, 1875 [7], 285; [8], 131; and 1877 [11], 300), the author confirms the results obtained by the last named, and assigns to the gum the formula $C_6H_{10}O_5$.

It is converted by boiling dilute sulphuric acid into dextrose (?), and after some days' boiling with a solution of potash into dextran (Scheibler, *ibid.*, 1875 [7], 287).

The gum is no doubt formed from the sugar in the beet in a manner analogous to the cellulosic fermentation described by Durin (this Journal, 1876, ii, 540). A. J. C.

Commercial Trimethylamine. By E. Duvillier and A. Buisine (*Compt. rend.*, **89**, 48—51).—Commercial trimethylamine prepared by the dry distillation of beet molasses, contains other substances besides trimethylamine. It is free from ammonia, and when treated with oxalic ether yields a dense white precipitate. The filtrate concentrated by distillation yields a further precipitate. These two precipitates are mixed, and separated by boiling water into three portions, one which is insoluble in hot water, but which melts and floats on the surface of the liquid, and solidifies like wax on cooling; another more soluble in hot water than the first; and a third still more soluble, especially in hot water.

The first body, which is di-isobutyloxamide, after recrystallisation from alcohol, is obtained in pearly needles, which melt in boiling water. The free base has a slightly aromatic odour, and yields a platinochloride crystallising in orange-coloured plates, and slightly soluble in water.

The second product crystallises from alcohol in pearly needles (m. p. 110°), and consists of dipropyloxamide. The free base gives an orange-coloured precipitate with platinum chloride.

By recrystallising the third product from water and alcohol, a granular substance is obtained, intermediate between dipropyloxamide and dimethyloxamide. The presence of the former body is probably the cause of the latter not crystallising in the ordinary manner. This body when decomposed with potash yields a base which forms a golden-yellow precipitate with platinum chloride, possessing all the properties of the methylamine compound described by Wurtz (*Ann. Chem. Phys.* [3], **30**, 457), and with which the results of the analyses correspond.

The bodies not precipitated by oxalic ether consist of di- and trimethylamine, and are contained in the mother-liquors (residue and distillate). The bases are distilled and collected in absolute alcohol, and the solution treated with oxalic ether. When the reaction has ceased, the liquid is distilled, and the unattacked base which distils over consists of trimethylamine.

The residue is dissolved in water, and caustic baryta is added; barium oxalate is precipitated, which is separated, and the excess of baryta precipitated with carbonic anhydride. The filtrate is evaporated, and the residue dissolved in alcohol at 80°. On cooling, an amorphous mass is left, perfectly insoluble in absolute alcohol, but

very soluble in water. It consists of barium dimethyl-oxamate, and on decomposition with potash yields dimethylamine, the double platinum salt of which forms octohedra.

It is therefore evident that commercial trimethylamine is not pure, as Vincent (*Bull. Soc. Chim.*, **29**, 194, and **217**, 151) declares it to be. The quantity of triethylamine present is but small, only from 5 to 10 per cent., that of the dimethylamine being about 50 per cent., whilst the remainder consists of methylamine, propylamine, and butylamine, in about equal proportions. L. T. O'S.

Distillation of Beetroot Residues. By C. Vincent (*Compt. rend.*, **89**, 238—240).—The products of the destructive distillation of the "vinasses," left after the distillation of the fermented molasses, vary with the degree of concentration of the liquid. In proportion as the amount of water present decreases, the quantity of ammonia increases, and the trimethylamine is replaced by mono- and dimethylamines. The "vinasses" from different localities yield varying proportions of gaseous and liquid products, which also vary in composition, methylic alcohol and the nitrils appearing to be the most variable constituents. These observations explain the results of Duvillier and Buisine's recent examination of *commercial trimethylamine.* C. H. B.

Action of Ethyl Chlorocarbonate on Mono- and Di-amylamine. By E. Custer (*Deut. Chem. Ges. Ber.*, **12**, 1328—1334).—*Ethyl monamyl carbamate*, $C_5H_{11}.NH.COOEt$, is formed by the action of ethyl chlorocarbonate (1 mol.) on an ethereal solution of amylamine (2 mols.). Amylamine hydrochloride separates out, leaving monamylurethane in solution. The pure urethane is a thick, colourless oil, soluble in alcohol and ether. Its sp. gr. is 0·93. When distilled with phosphoric anhydride it yields *amyl cyanate*, which is a mobile volatile liquid boiling at 134°, combining with alcohol to form urethane, and with triethylphosphine to form amyl cyanurate. When it is mixed with strong hydrochloric acid, white crystalline scales of amylamine hydrochloride separate out.

Monamylcarbamide, $NH_2.CO.NH.C_5H_{11}$, is obtained in the form of an oily liquid, which solidifies on standing to a colourless crystalline mass (m. p. 88—91°), by digesting amyl cyanate with excess of ammonia. The carbamide and its nitrate are sparingly soluble in water.

Diamylcarbamide, $CO(NH.C_5H_{11})_2$, formed by digesting amyl cyanate with an alcoholic solution of amylamine, crystallises in white needles, which melt at 39° and boil at 270°. The crystals are soluble in alcohol and ether.

Triamylcarbamide, $NH.C_5H_{11}.CO.N(C_5H_{11})_2$, is a colourless syrupy liquid, boiling at 260°.

Tetramylcarbamide, $N(C_5H_{11})_2.CO.N(C_5H_{11})_2$, an oily liquid (b. p. 240°), is formed by the action of ethyl chlorocarbonate on diamylamine. Diamylurethrane is probably formed in the first instance, and this is converted into tetramylcarbamide, by the action of the excess of diamylamine thus:—

$$(C_5H_{11})_2N.COOEt + NH(C_5H_{11})_2 = N(C_5H_{11})_2.CO.N(C_5H_{11})_2 + C_2H_6O.$$

The compound is soluble in alcohol and ether; it is decomposed by alkalis, forming carbonic anhydride and the diamine base.

Ethyl diamylcarbamate, $(C_5H_{11})_2N.COOEt$, is prepared by the action of ethyl chlorocarbonate on pure diamylamine. It is an oily liquid, lighter than water, soluble in alcohol and ether, remaining liquid at $-20°$ and boiling at 246—247°.

Pure diamylamine.—The author prepares pure diamylamine from the fraction boiling above 130°, obtained in the preparation of amylamine. For this purpose it is converted into the hydrochloride, mixed with an equal quantity of sodium nitrite, and boiled with dilute alcohol for 24 hours. The crystalline mass of nitrosodiamylamine, which forms on cooling, is washed with water and with ether, and decomposed by distillation with soda. Pure diamylamine boils at 187°, and not at 180° as stated by Silva. W. C. W.

Salts of Guanidine. By L. Jousselin (*Compt. rend.*, **88**, 1086).—The author's method of preparing guanidine nitrate dispenses with the preliminary preparation of the carbonate. He rubs dried thiocyanate of guanidine in a mortar with pure nitric acid diluted with $\frac{1}{10}$th of water. The liquid soon becomes pasty again from the deposition of the nitrate, and it must then be immediately thrown on to a vacuum filter, formed of a plug of asbestos, whereby the mother-liquid is removed. It is necessary to effect the mixture rapidly, otherwise a deflagration ensues.

The carbonate of guanidine is prepared by treating the thiocyanate with diluted sulphuric acid, and boiling. Sulphocyanic acid is driven off, and some perthiocyanic acid is deposited on cooling. On treating the clear acid solution with excess of barium carbonate, filtering, and allowing it to evaporate spontaneously, it yields guanidine carbonate.

By dissolving the carbonate in a measured quantity of diluted sulphuric acid, and then adding that quantity of baryta-water which will exactly remove the sulphuric acid, free guanidine may be obtained. When guanidine nitrate is treated with concentrated sulphuric acid, nitrous vapours are evolved, and the residue, after being drained on a porous tile and recrystallised from water, yields nitrosoguanidine. R. R.

Chloral Hydrate. By A. Wurtz (*Compt. rend.*, **89**, 190—192).—Experiments made two years ago led the author to suppose that when chloral vapour and steam were brought together under such conditions that chloral hydrate could not condense, an absorption of heat took place. A repetition of these experiments, with modified apparatus has, however, shown that such is not the case, and that when vapour of chloral and steam are brought together under the above conditions, there is no thermal disturbance whatever. The dissociation of chloral hydrate is complete at 100° at the ordinary pressure, and even at 61° under a pressure of 9 mm. C. H. B.

Action of Boron Fluoride on Acetone. By F. H. Landolph (*Compt. rend.*, **89**, 173—175).—The following substances are obtained by the action of boron fluoride on acetone:—(1.) *Fluoboracetone* α:

$C_3H_6O.3HF.B_4O_4$, a mobile, limpid liquid, boiling at 120—123°. (2.) *Fluoboracetone β*: $C_3H_6O.3HF.B_4O_4$, crystallising in thin, brilliant, white plates, which melt at 36°, and boil at 90—92°. (3.) *Boracetone*, $C_3H_6O.B_2O_2H_2$, a limpid, very mobile, and volatile liquid, boiling at 50°. These compounds burn with a green flame, and when exposed to the air evolve white, irritating, strongly acid fumes. They are decomposed by water, with formation of boric acid, and volatile bodies having an agreeable odour. Dry oxygen gives characteristic oxidation products, and sodium gives sodium fluoride and gaseous compounds. (4.) Small quantities of hydrocarbons having the formulæ C_9H_{14} and C_9H_{18}, which boil at 162—165° and 130° respectively. The formula of *fluorborethylene*, previously described by the author, is $C_2H_4.HF.BO_2$. C. H. B.

Action of Acetic and Sulphurous Anhydrides on Aluminium Chloride. By A. Adrianowsky (*Deut. Chem. Ges. Ber.*, **12**, 853).—A compound having the formula $AlCl_3SO_2$ is obtained by the action of sulphurous anhydride on aluminium chloride. It is a very thick, oily liquid, of a pale-red colour, and at −10° solidifies to a glassy mass. By heating in closed tubes at 100°, it attains the consistence of anhydrous glycerol, and at higher temperatures decomposes, giving aluminium chloride, sulphurous anhydride, and small quantities of sulphur chlorides and aluminium sulphate. It is rapidly attacked by water, with evolution of sulphurous anhydride. It is decomposed by benzene, even at the ordinary temperature, with formation of hydrochloric acid: this reaction takes place much more readily in presence of aluminium chloride. After treating the products of the reaction first with water and then with hydrochloric acid, we obtain benzenesulphinic acid, $C_6H_5.SO_2H$, thus:—

(1.) $AlCl_2.SO_2Cl + C_6H_6 = HCl + AlCl_2.SO_2.C_6H_5$.
(2.) $AlCl_2.SO_2.C_6H_5 + 2H_2O = Al(OH)_2SO_2.C_6H_5 + 2HCl$.
(3.) $Al(OH)_2SO_2.C_6H_5 + 6HCl = Al_2Cl_6 + 2(C_6H_5.SO_2H) + 6H_2O$.

T. C.

Compounds of Ethyl Monochloracetoacetate with Metals. By F. Allihn (*Deut. Chem. Ges. Ber.*, **12**, 1298—1300).—When an ammoniacal solution of copper sulphate is shaken up with ethyl monochloracetoacetate, a green precipitate separates out, which has the composition $Cu(C_6H_8ClO_3)_2$. The compound is deposited from solution in carbon bisulphide in glistening green plates, which are soluble in alcohol, ether, benzene, acetone, acetic ether, and chloroform. Ethyl dichloracetoacetate does not combine with copper. *Magnesium ethyl monochloracetoacetate* forms silky needles, soluble in alcohol. *Nickel ethyl monochloracetoacetate* is a pale-green, and the cobalt compound a pale rose-coloured powder. W. C. W.

Conversion of Furfurangelic Acid into Azelaic Acid. By P. Toennies (*Deut. Chem. Ges. Ber.*, **12**, 1200—1202).—Baeyer and the author (*Ber.*, **10**, 1364), have shown that the anhydride of normal butyric acid forms with furfural a condensation product, $C_9H_{10}O_3$, to

which they gave the name of furfurangelic acid. This acid on reduction with sodium amalgam gives *furfurvaleric acid*, $C_4H_3O(CH_2)_4.COOH$, which is a colourless oil of unpleasant odour, and can be distilled without decomposition. On treatment with bromine-water, it yields an aldehyde, which by the action of silver oxide is converted into *butyrofuronic acid*, $COOH.CH:CH.CO.(CH_2)_4.COOH$, homologous with furonic acid (Baeyer, *ibid.*), thus :—

$$(1.)\ \underset{\text{Furfurvaleric acid.}}{C_9H_{12}O_3} + Br_2 + H_2O = \underset{\text{Aldehyde of butyrofuronic acid.}}{C_9H_{12}O_4} + 2HBr.$$

$$(2.)\ C_9H_{12}O_4 + Ag_2O = \underset{\text{Butyrofuronic acid.}}{C_9H_{12}O_5}.$$

Butyrofuronic acid (m. p. 141°) is easily soluble in water, alcohol, and warm chloroform, but little soluble in ether. On reduction with sodium amalgam it gives first the acid $COOH.(CH_2)_2.CO.(CH_2)_4.COOH$, and then normal azelaic acid $COOH.(CH_2)_2.CH(OH).(CH_2)_4.COOH$, which separates from solution in chloroform in slender needles (m. p. 118°) : this is probably isomeric with the azelaic acid previously known (m. p. 106°). T. C.

Formation of Glycollic and Pyruvic Acids from Tartaric Acid. By G. Bouchardat (*Compt. rend.*, **89**, 99—101).—By the action of concentrated sulphuric acid on tartaric acid at 40° to 50°, a mixture of 4 vols. carbonic oxide to 1 vol. sulphurous anhydride, containing about 2 to 4 per cent. of carbonic anhydride, is evolved; towards the end of the reaction, the quantity of carbonic anhydride increases. The residue is dissolved in water, and baryta-water is added, the solution is then filtered, and the filtrate evaporated, when crystals of barium tartrate and racemate separate out. On saturating again with baryta and filtering, the filtrate on evaporation leaves a non-crystalline mass of barium glycollate and pyruvate. The acids are liberated by sulphuric acid and converted into the calcium salts; on evaporation, calcium glycollate separates out whilst calcium pyruvate remains in solution, from which it may be extracted, by treating with sulphuric acid and agitation with ether. It does not crystallise, and is very soluble in water; it partially decomposes by distillation, giving rise to pyrotartaric acid. With the exception of the copper salt, the salts of pyruvic acid do not crystallise.

The formation of pyruvic acid from tartaric acid is explained thus : $C_4H_6O_6 = H_2O + CO_2 + C_3H_4O_3$.

The formation of glycollic acid may be explained thus: tartaric acid contains the formyl group twice; this group by the action of concentrated sulphuric acid loses carbonic oxide and water, and a compound having the composition of glyoxal is formed; and this assimilates the elements of water, with formation of glycollic acid :—

$$C_4H_6O_6 = 2CO + 2H_2O + C_2H_2O_2.$$
$$C_2H_2O_2 + H_2O = C_2H_4O_3.$$ L. T. O'S.

Malonic Acid. By H. v. Miller (*J. pr. Chem.* [2], **19**, 326—

331).—The author finds that malonic acid is best prepared by treating a concentrated solution of potassium monochloracetate with potassium cyanide, not in excess, and decomposing the potassium cyanoacetate so obtained by potash.

Potassium malonate forms large transparent monoclinic crystals, containing 2 mols. of water: this it loses at 175°.

It is decomposed by sulphuric acid, with separation of pure malonic acid, which may be extracted by agitation with ether. When an aqueous solution of potassium malonate is subjected to electrolysis, carbonic anhydride, hydrogen, and small quantities of ethylene are produced. M. M. P. M.

Preparation of Pure Tartaric Acid. By O. Ficinus (*Arch. Pharm.* [3], **14**, 310—311).—As neither the decomposition of calcium tartrate by sulphuric acid, nor of lead tartrate by sulphuretted hydrogen, is sufficient for the perfect purification of tartaric acid, the decomposition of the zinc salt is recommended. Crude tartaric acid is saturated with calcium carbonate, the calcium salt is then digested with zinc chloride, and the resulting zinc tartrate treated with sulphuretted hydrogen: the filtrate on evaporation yields pure tartaric acid.

E. W. P.

Action of Phosphorus Pentachloride on Saccharic Acid, Mannitol, &c. By C. J. Bell (*Deut. Chem. Ges. Ber.*, **12**, 1271—1275).—According to Wichelhaus (*Annalen*, **135**, 252), no organic chloride is formed when phosphorus pentachloride acts on cadmium saccharate. By substituting the potassium for the cadmium salt, however, the author has obtained chloromuconic acid, $C_6H_4Cl_2O_4$. It is easily soluble in alcohol, crystallising from it in long, silky needles, and is sparingly soluble in ether and in water. It melts at 260°, and is at the same time partially decomposed. Comparison of the ethyl salt of this acid, and that of the chloromuconic acid from mucic acid, show these acids to be identical.

Mannitol heated at 140° in an oil-bath, with more than 6 mols. phosphorus pentachloride, and the product distilled in steam, yields a slightly yellowish oil of the composition $C_6H_6Cl_4$. It is decomposed by distillation, and is reduced by hydriodic acid.

Dulcite yields the same product, but in somewhat larger quantities; when this chloride is heated in sealed tubes with hydriodic acid and amorphous phosphorus, it yields a small quantity of volatile hydrocarbon, probably hexane.

Erythrol, quercite, and sorbite yield a similar oil; which the author styles mannitotetrachlorhexin; its formation may be explained thus:—

$$CH_2(OH).(CH.OH)_4.CH_2(OH) + 6PCl_5 = CH_2Cl.(CHCl)_4.CH_2Cl + 6POCl_3 + 6HCl.$$

$$\underset{\text{Hypothetical mannitol chloride.}}{CH_2Cl.(CHCl)_4.CH_2Cl} - 2HCl = \underset{\text{Mannitotetrachlorhexin.}}{CH_2Cl.CCl:CH.CH:CCl.CH_2Cl}.$$

P. P. B.

Ethyl Formyltricarbonate. By M. Conrad (*Deut. Chem. Ges. Ber.*, **12**, 1236—1237).—Ethyl formyltricarbonate is prepared by the action of ethyl chlorocarbonate on ethyl-sodium malonate (this vol., p. 707). It is a colourless liquid of agreeable odour, insoluble in water, boiling between 254° and 260°. Its sp. gr. is 1·1 at 19° (water at 15° = 1). By saponification this compound yields malonic acid, as shown by analysis of the free acid and of its silver salt: $CH(COOEt)_3 + 4KOH = CH_2(COOK)_2 + K_2CO_3 + 3EtHO$.

From this it would seem that the existence of formyltricarbonic acid in the free state is highly improbable. P. P. B.

Relation of Dibromopyromucic Acid to Mucobromic Acid. By P. Toennies (*Deut. Chem. Ges. Ber.*, **12**, 1202—1204).—Dibromopyromucic acid, $C_5H_2Br_2O_3$, on treatment with bromine-water *in the cold*, gives carbonic anhydride, and *mucobromic aldehyde*, $C_4H_2Br_2O_2$: this crystallises from ether in stellate groups of needles (m. p. 88°), which are easily soluble in water, ether, and chloroform. On gently warming it with chromic acid solution, or boiling it with bromine water, it takes up an atom of oxygen, yielding mucobromic acid, $C_4H_2Br_2O_3$. This reaction is analogous to the action of bromine water in the cold on pyromucic acid, whereby fumaraldehyde is formed (Limpricht), except that in the latter the action takes place at the ordinary temperature, whereas in the former heat is required. From this it follows that mucobromic acid is a substitution product of fumaraldehyde, $C_4H_4O_3$. T. C.

Stannopropyls and Stannisopropyls. By A. Cahours and E. Demarçay (*Compt. rend.*, **88**, 1112—1117).—The action of pure tin on propyl iodide gives rise to the di-iodide of stannopropyl, whilst that of an alloy of tin with 10 per cent. of sodium gives rise to the moniodide of tristannopropyl. The former compound, $Sn(C_3H_7)_2I_2$, cannot well be separated by distillation from the other products of the reaction, unless the operation is conducted in a vacuum. The di-iodide of stannopropyl is a colourless highly refracting liquid, b. p. 270—273°. Alkalis cause the separation of a white amorphous substance, insoluble in water, alcohol, or ether. This is the oxide of stannopropyl, which is converted by hydrochloric acid into dichloride of stannopropyl, $Sn(C_3H_7)_2Cl_2$ (m. p. 80—81°). It yields also crystalline salts with other acids.

When instead of pure tin an alloy containing 10 per cent. of sodium is used, the iodide of tristannopropyl is produced, and may be dissolved out of the product by ether. On distilling the residue left by evaporation of the ethereal solution, a colourless mobile liquid (b. p. 260—262°) of a very pungent odour, is obtained. Its composition is $Sn(C_3H_7)_3.I$, and at the contact of silver salts it is decomposed, yielding AgI and a salt of $Sn(S_3H_7)_3$. Distilled with potash, it yields a crystalline hydroxide, $Sn(C_3H_7)_3HO$, which combines with acids to produce well-defined crystallised salts.

By substituting isopropyl iodide for propyl iodide, a series of isopropyl compounds exactly analogous to the former series is obtained by the same reactions. The fusibility and volatility of the isopropyl compounds are greater than those of their isomerides, con-

formable to what is observed in the other compounds of the same radicals. The *iodide*, $Sn(C_3H_7)_2I_2$, boils at 265—268°. The *chloride* melts at 56·5—57·5°. The *iodide*, $Sn(C_3H_7)_3I$, boils at 256—258°.

R. R.

Stannobutyl and Stannoamyl Iodides. By A. Cahours and E. Demarçay (*Compt. rend.*, **89**, 68—73).—*Stannic di-iodo-diisobutide*, $Sn(C_4H_9)_2I_2$, is a colourless liquid, boiling at 290—295°, obtained by heating tinfoil and isobutyl iodide to 120—125° in a sealed tube for several hours. Ammonia and potash give a white amorphous precipitate of the hydroxide, which yields crystalline compounds with acids. The corresponding chlorine compound, $Sn(C_4H_9)_2Cl_2$, prepared by the action of hydrochloric acid on the iododerivative, is a colourless, mobile, heavy liquid, boiling at 260—262° and solidifying at 5—6° to a mass of silky needles resembling asbestos. *Stannic iodo-tributide*, $Sn(C_4H_9)_3I$, a colourless liquid, having an irritating odour, is obtained by heating a finely powdered alloy of tin and sodium, containing 8 to 10 per cent. of the latter metal, with an excess of isobutyl iodide and exhausting the solidified mass with ether. It boils at 284—286°, and when heated with potash gives the corresponding hydroxide, which boils at 311—314°, and forms crystalline compounds with formic and acetic acids.

The action of amyl iodide on tin appears to yield a mixture of *stannic di-iodo-dipentide* and *stannic iodo-tripentide*, which decomposes on distillation, and when treated with ammonia gives a white flocculent precipitate of the two hydroxides, which may be separated by means of ether, and yield crystalline compounds with acids. When an alloy of sodium and tin is employed, the main product of the reaction is *stannic iodo-tripentide*, $Sn(C_5H_{11})_3I$, an almost colourless liquid, having a feebly irritating odour and boiling at 302—305°. The action of potash yields the hydroxide $Sn(C_5H_{11})_3OH$, a colourless, limpid, heavy liquid, which boils at 335—338° with partial decomposition, and forms crystalline compounds with formic and acetic acids.

Passing from the stannic methides to the stannic pentides, the stability of the compounds gradually decreases and their odour becomes less irritating.

C. H. B.

Separation of Orthoxylene from its Isomerides, and a New Xylidine. By E. Wroblewsky (*Deut. Chem. Ges. Ber.*, **12**, 1226—1229).—This separation consists in the conversion of xylene from coal-tar oils into the amine derivative; this is then heated with acetic acid for some days, and the resulting acetyl compound fractionated, The part boiling above 320° is metacetoxylide; the portion boiling below 310°, and consisting of acetic acid, water, and unaltered xylidine acetate, is heated with caustic soda, the oily base thus liberated being again treated with acetic acid and the product fractionated as before. The portion boiling below 310° thus obtained yields the new xylidine, which is a derivative of orthoxylene, having the constitution $C_6H_3(CH_3)_2.NH_2$ [1.2.4]. It is a colourless liquid, which becomes brown on standing and smells like aniline. It boils at 215° and does not solidify at 20°; its sp. gr. is 0·9942 at 20°. The hydrochloride, $C_6H_3(CH_3)_2NH_2.HCl + \frac{1}{2}H_2O$, is easily soluble in water and

crystallises in large, thick tables, which may be sublimed. It is precipitated from its aqueous solutions by concentrated hydrochloric acid.

The nitrate, $C_6H_3(CH_3)_2.NH_2.HNO_3$, crystallises in large, rhombic tables, which are easily coloured rose; 2·7 parts of the salt are soluble in 100 parts of water.

The acid sulphate, $C_6H_3(CH_3)_2.NH_2.H_2SO_4 + 2\frac{1}{2}H_2O$, is very easily soluble in water; crystallises in large, white, shining tables.

Acetoxylide, $C_6H_3(CH_3)_2.NH.C_2H_3O$, obtained by the action of acetic chloride on a solution of the base in acetic acid, is soluble in water and very soluble in alcohol and acetic acid. It crystallises from the alcoholic solution in white, shining tables, melting at 131—132°.

The new xylidine, when treated with nitrous acid, yielded a nitro-compound, m.p. 56°, identical with that which Jacobsen obtained by the nitration of orthoxylene. This, together with the method of preparing this xylidine and a comparison with the other known xylidines, show the new xylidine to be a derivative of orthoxylene. P. P. B.

Paradiethylbenzene from Paradibromobenzene. By H. Aschenbrandt (*Deut. Chem. Ges. Ber.*, **12**, 1303—1306).—*Paradiethylbenzene*, prepared by the action of sodium on a mixture of paradibromobenzene and ethyl iodide, boils at 181—182° and remains liquid in a freezing mixture.

Paradiethylbenzenemonosulphonic acid is a thick syrupy liquid, which could not be solidified by cold. Its salts, however, crystallise remarkably well.

Mononitroparaethylbenzoic acid is prepared by dropping ethylbenzoic acid into cold fuming nitric acid. It is also formed as a bye-product in the preparation of ethylbenzoic acid by the action of dilute nitric acid on paradiethylbenzene. Nitroparaethylbenzoic acid is deposited in needle-shaped crystals from its solutions in ether and hot water, and it separates out in prisms from its solutions in alcohol, chloroform, and benzene. The acid melts at 156° and sublimes at a higher temperature. The *barium* salt, $(C_9H_8O_4N)_2Ba + 4H_2O$, forms small glistening scales; the *calcium* salt, $(C_9H_8O_4N)_2Ca + 2H_2O$, crystallises in broad needles; the *strontium* salt forms pale yellow plates, containing 4 mols. H_2O. These three salts are sparingly soluble in water. The *sodium* salt, $C_9H_8O_4NNa + 2H_2O$, crystallises in large, lustrous plates, which dissolve freely in water.

The author points out that the diethylbenzene, prepared synthetically by Fittig and König (*Annalen*, **144**, 285), consists of a mixture of ortho- and para-diethylbenzene. W. C. W.

Action of Sulphochlorides on Amines. By W. Michler and G. Moro (*Deut. Chem. Ges. Ber.*, **12**, 1168—1171).—When trichlormethylsulphochloride is added in small portions at a time to warm dimethylaniline, tetramethyldiamidobenzophenone and tetramethyldiamidodiphenylmethane are obtained, the formation of the first compound being represented by the equations:—

(1.) $2NMe_2.C_6H_5 + CCl_3.SO_2Cl = SO_2 + 2HCl + CCl_2(C_6H_4.NMe_2)_2$.
(2.) $CCl_2(C_6H_4.NMe_2)_2 + H_2O = CO(C_6H_4.NMe_2)_2 + 2HCl$.

Tetramethyldiamidobenzophenone, $CO(C_6H_4.NMe_2)_2$, forms rhombic crystals (m. p. 152°), which are easily soluble in alcohol and ether. It has basic properties, and forms a well-crystallised platinochloride, $CO(C_6H_4.NMe_2)_2.H_2PtCl_6$. A compound isomeric with tetramethyldiamidobenzophenone has been previously obtained by the action of carbonic chloride on dimethylaniline.

Tetramethyldiamidodiphenylmethane, $CH_2(C_6H_4.NMe_2)_2$, crystallises from alcohol in large, colourless plates (m. p. 91) and is identical with the compound obtained by Hanhardt (*Ber.*, **12**, 674) from tetrachloromethane and dimethylaniline, and with that prepared by Doebner (*Ber.*, **12**, 810) from dimethylaniline and methylene iodide. On heating with sulphuric acid and potassium dichromate it smells strongly of quinone. It forms a platinochloride, $CH_2(C_6H_4.NMe_2)_2H_2PtCl_6$, and dissolves in methyl iodide with the formation of a crystalline compound, having the composition $CH_2(C_6H_4.NMe_2)_2.2MeI$. On treating this with freshly precipitated silver chloride the corresponding chlorine compound $CH_2(C_6H_4.NMe_2).2MeCl$ is obtained; it crystallises in needles and is easily soluble in water. On dissolving the base in alcohol and adding to the acidified solution a concentrated solution of sodium nitrite, a nitroso-compound is produced which crystallises from alcohol in yellow needles (m. p. 165°).

The formation of basic compounds by the action of sulphochlorides on dimethylaniline appears to be a general reaction, and has been found to occur in the case of benzene-, toluene-, α-, and β-naphthalene-sulphochlorides, the product obtained from each being apparently identical with tetramethyldiamidodiphenylmethane. This same base is also produced by the action of phosphorus pentachloride on dimethylaniline. T. C.

Benzylamine. By C. Rudolph (*Deut. Chem. Ges. Ber.*, **12**, 1297).—*Benzylamine* (b. p. 185°) may be obtained by the action of alcoholic potash on benzylacetamide (m. p. 57°) prepared from acetamide and benzoic chloride. Benzylamine hydrochloride is deposited from an alcoholic solution in large plates. The platinochloride crystallises in orange-coloured plates, and the sulphate forms transparent crystals, freely soluble in water. W. C. W.

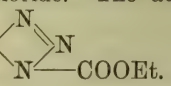
Derivatives of Orthonitraniline. By C. Rudolph (*Deut. Chem. Ges. Ber.*, **12**, 1295—1297).—*Orthonitrophenylurethane* is formed by heating a chloroform solution of orthonitraniline with ethyl chlorocarbonate. On recrystallisation from light petroleum, it is obtained in long yellow prisms which melt at 58°.

Orthamidophenylurethane hydrochloride, produced by the action of tin and hydrochloric acid on the preceding compound, crystallises in large, colourless anhydrous plates.

Orthamidophenylurethane separates out as a crystalline powder on the addition of an alkali to the aqueous solution of the hydrochloride. By recrystallisation from water or from a mixture of ether and light petroleum, it can be obtained in long colourless needles resembling

asbestos in appearance. The base melts at 86°, but decomposes at a higher temperature, yielding orthophenylenecarbamide—

$$C_6H_4(NH_2).NH.COOEt = C_6H_4(NH)_2CO + EtHO.$$

The carbamide is deposited from an alcoholic or aqueous solution in small colourless plates (m. p. 305°). A crystalline precipitate is formed on the addition of potassium nitrite to an aqueous solution of orthamidophenylurethane hydrochloride. The author represents its constitution by the formula .

W. C. W.

Decomposition of Phenylethylamine Hydrochloride. By M. Fileti and A. Piccini (*Deut. Chem. Ges. Ber.*, **12**, 1308).—When phenylethylamine hydrochloride is heated at its boiling point (217°) it decomposes, forming diphenylethylamine hydrochloride, styrene, and ammonium chloride. The following reactions take place:—

(1.) $2(Ph.CH_2.CH_2.NH_2.HCl) = NH_4Cl + (Ph.CH_2.CH_2)_2NH.HCl.$
(2.) $Ph.CH_2.CH_2.NH_2.HCl. = NH_4Cl + Ph.CH:CH_2.$

W. C. W.

Nitration of Benzenesulphanilide. By W. Michler and G. Blattner (*Deut. Chem. Ges. Ber.*, **12**, 1167—1168).—*Trinitrobenzenesulphanilide*—

$$C_6H_4(NO_2).SO_2.NH.C_6H_3(NO_2)_2 \text{ or } C_6H_3(NO_2)_2.SO_2.NH.C_6H_4(NO_2),$$

is obtained, together with ortho- and meta-mononitrobenzenesulphonic acids, by acting on benzenesulphanilide with fuming nitric acid. It crystallises in pale yellow needles (m. p. 210°), which are sparingly soluble in cold alcohol, but more easily soluble in boiling alcohol and in glacial acetic acid. T. C.

Amidines and Thiamides of Monobasic Organic Acids. By A. Bernthsen (*Liebig's Annalen*, **197**, 341—350).—Wallach obtained a series of sulphur compounds isomeric with the thiamides by acting on sodium thiacetanilide and on thiacetanilide with ethyl bromide or methyl iodide (*Ber.*, **11**, 1590). Pinner and Klein also obtained a chloride by the action of gaseous hydrochloric acid on a mixture of benzonitrile and amylmercaptan (*Ber.*, **11**, 1825). The author thinks that the bodies he has obtained by the action of methyl iodide and ethyl bromide on phenylthiacetamide (*Annalen*, **192**, 57), belong to the same class.

Phenylacetimidothioethyl ether, $C_6H_5.CH_2.C(S.C_2H_5):NH$, is prepared by acting on phenylthiacetamide with ethyl iodide, at a temperature below 100°. When the iodide thus obtained is treated with soda solution, it yields an oily body, probably $C_{10}H_{13}NS$, which is very unstable, and splits up on heating into mercaptan and benzyl cyanide. The same body may also be obtained by the action of hydrochloric acid on a mixture of benzylcyanide and mercaptan.

Benzimidothioethyl ether, $C_6H_5.C(S.C_2H_5):NH$.—By the action of ethyl iodide on thiobenzamide, a crystalline hydriodide is obtained;

it is similar to the compound formed from phenylthiacetamide, but is much more stable. On decomposition it yields benzonitrile and mercaptan.

Benzimidothiobenzyl ether, $C_6H_5.C(S.C_7H_7) : NH$, is obtained as hydrochloride by heating thiobenzamide with benzyl chloride, or benzonitrile and benzylsulphydrate with hydrochloric acid gas.

G. T. A.

Diethyl- and Diamyl-anhydrobenzyldiamidobenzene Compounds. By H. Hübner and E. Simon (*Deut. Chem. Ges. Ber.*, **12**, 1342—1344). — *Diethylanhydrobenzyldiamidobenzene tri-iodide*, $C_6H_4 : N_2C.C_6H_5(C_2H_5)_2I_3$ (m. p. 154°), is obtained in reddish-brown plates or needles, soluble in alcohol, by the action of ethyl iodide on anhydrobenzyldiamidobenzene at 210°. On boiling the alcoholic solution with lead hydroxide, *diethylanhydrobenzyldiamidobenzene iodide*, $C_{17}H_{19}N_2I$, separates out in yellow needles, which dissolve in water, with partial decomposition. *Diethylanhydrobenzyldiamidobenzene hydroxide*, $C_{17}H_{19}N_2OH$ (m. p. 132°), prepared by the action of an alkali on the preceding compound, is soluble in alcohol, benzene, chloroform, and low boiling petroleum (b. p. 50—80°). From this base, the following salts were obtained:—$C_{17}H_{19}N_2Cl.2H_2O$, crystallises in colourless plates, which lose their water of crystallisation at 125°. $(C_{17}N_{19}N_2Cl)_2PtCl_4$ forms small orange-coloured crystals, and $C_{17}H_{19}N_2O.SO_2.OH.H_2O$ yields colourless thick plates. The nitrate is an oily liquid, which has not been solidified.

Diamylanhydrobenzyldiamidobenzene tri-iodide, $C_{23}H_{31}N_2I_3$, forms dark, reddish-brown plates, which melt at 111—112°. *Diamylanhydrobenzyldiamidobenzene hydroxide*, $C_{23}H_{31}N_2.OH$, is deposited from an alcoholic solution in colourless crystals, which are soluble in benzene, ether, chloroform, and petroleum (b. p. 80—100°). When quickly heated, the base melts at 80°; but if the temperature is raised slowly, it melts at 90°. The following salts were prepared:—$C_{23}H_{31}N_2Cl.HCl.H_2O$ forms thick, colourless crystals; $(C_{23}H_{31}N_2Cl)_2PtCl_4$ separates out as an orange-coloured precipitate on the addition of platinum chloride to a solution of the chloride. The nitrate, $C_{23}H_{31}N_2(NO_3).HNO_3$, crystallises in colourless plates, which melt at 90°.

W. C. W.

Ethers of Trinitrophenol. By C. Willgerodt (*Deut. Chem. Ges. Ber.*, **12**, 1277—1279).—The ethyl ether already described by Müller and Stenhouse (*Annalen*, **141**, 79) may be obtained by treating an alcoholic solution of picryl chloride, $C_6H_2(NO_2)_3Cl = [6.4.2.1]$, with an alcoholic potash solution in the cold. The chief reaction is $C_6H_2(NO_2)_3Cl + KOH + EtOH = C_6H_2(NO_2)_3.OEt + KCl + H_2O$. Potassium picrate and hydrochloric acid are also formed; the former is separated by its insolubility in alcohol, from which the ether after repeated crystallisation is obtained in long, colourless needles, m. p. 78°. The author, by the use of barium hydrate and sodium carbonate, has tried in vain to obviate the regeneration of trinitrophenol. The phenyl ether, $C_6H_2(NO_2)_3.OPh$, separates out in white needles from an alcoholic solution of picryl chloride after treatment with an alcoholic solution of potassium phenylate.

The author has also observed the formation of ordinary ether, when alcoholic solutions of ethyl iodide and of potash are mixed at ordinary temperatures. P. P. B.

New Colouring Matter from Orthamidophenol. By G. Fischer (*J. pr. Chem.* [2], **19**, 317—321).—Orthamidophenol does not yield an azophenol on treatment with oxidising agents; its behaviour is not therefore analogous to that of amidobenzene, which yields azobenzene when treated with potassium permanganate or bleaching powder.

When orthamidophenol hydrochloride is treated with bleaching powder, an amorphous, humus-like substance is obtained, which yields red crystals on heating. The red crystals are obtained in larger quantity by using potassium ferricyanide as oxidising agent. The new colouring matter appears to have the formula $C_{24}H_{10}N_3O_2$; it exhibits feebly basic characters, forming brilliantly coloured solutions with acids. The substance is now undergoing thorough examination.

M. M. P. M.

Constitution of Dichlorazophenol. By R. Schmitt (*J. pr. Chem.* [2], **19**, 312—317).—The author confirms the opinion of Hirsch, that the compound prepared by himself and Bennewitz, in 1874 (this Journal [2], **12**, 260) and described as dichlorazophenol, is really *chloroquinonimide*, $C_6H_3Cl.ONH$. The vapour-density could not be determined, as the compound decomposes a few degrees above its melting point: hence an indirect method of determining the molecular weight was adopted. Hirsch laid stress on the fact that the supposed dichlorazophenol yielded dichloramidophenol when acted on by hydrochloric acid, and concluded that it could not therefore have the constitution of an azo-compound. The author, however, shows that parazophenetol yields paramidochlorophenol, and that azobenzene yields parachloraniline (among other products) when heated in sealed tubes with concentrated hydrochloric acid.

In conclusion, the author states that paramidophenol yields almost the theoretical quantity of quinone when the sulphate is dissolved in water acidulated with sulphuric acid, and lead peroxide is added until the violet colour disappears which is produced at first. The quinone may then be extracted by agitation with ether. M. M. P. M.

Relation between the Xylenols, Homo-oxybenzyl Alcohols, Hydroxytoluic Aldehydes, Hydroxytoluic Acids, Alcohol-hydroxybenzoic Acids, Aldehyde-hydroxybenzoic Acids, and Hydroxyphthalic Acids. By F. Tiemann (*Deut. Chem. Ges. Ber.*, **12**, 1338—1342).—The author has arranged these compounds in a tabular form, showing their melting and boiling points:—

Xylenols, $C_6H_3(Me).(Me).(OH)$	Ortho (1 : 2 : 4), m. p. 61°, b. p. 225°	α-Metaxylenol (1 : 3 : 4), b. p. 211·5°
Homo-oxybenzyl alcohol $C_6H_3.Me(CH_2OH).OH$	—	Parahomosaligenin, m. p. 105°
Hydroxytoluic aldehydes $C_6H_3(COH)Me(OH)$	Metahomoparahydroxybenzaldehyde (1 : 2 : 4), m. p. 110°	Parahomosalicylaldehyde (3 : 1 : 4), m. p. 56°, b. p. 217°
		Orthohomoparahydroxybenzaldehyde (1 : 3 : 4), m. p. 115°
Hydroxytoluic acids $C_6H_3(COOH)(Me)(OH)$	Metahomoparahydroxybenzoic (1 : 2 : 4), m. p. 177—178°	Parahomosalicylic (3 : 1 : 4), m. p. 151°
		Orthohomoparahydroxybenzoic (1 : 3 : 4), m. p. 172°
Alcohol hydroxybenzoic acids .. $C_6H_3(CH_2OH)(COOH)(OH)$	—	Parahydroxymethylsalicylic acid (1 : 3 : 4), decomposes at 160°
		Orthohydroxymethylparaoxybenzoic acid (3 : 1 : 4), m. p. above 270°
Aldehyde hydroxybenzoic acids $C_6H_3(COH)(COOH)(OH)$	Para-aldehydometahydroxybenzoic acid (1 : 2 : 4), decomposes on distillation	Para-aldehydosalicylic (1 : 3 : 4), m. p. 248—249°
		Orthaldehydoparahydroxybenzoic (3 : 1 : 4), m. p. 243°
Hydroxyphthalic acids $C_6H_3(COOH)(COOH)(OH)$	Hydroxyorthophthalic acid (1 : 2 : 4), m. p. 181°	α-Hydroxyisophthalic acid (1 : 3 : 4), melts above 380°

Xylenols	β-Metaxylenol (1 : 3 : 4), m. p. 74·5°, b. p. 211°	Paraxylenol (1 : 4 : 3), m. p. 74·5°, b. p. 211·5°
Hydroxytoluic aldehydes	Orthohomosalicylaldehyde (3 : 1 : 2), m. p. 17°, b. p. 208—209°	Metahomosalicylaldehyde (4 : 1 : 3), m. p. 54°, b. p. 222°
Hydroxytoluic acids	Orthohomosalicylic acid (3 : 1 : 2), m. p. 162°	Metahomosalicylic acid (4 : 1 : 3), m. p. 173°
		Orthohomomethydroxybenzoic acid (1 : 4 : 3), m. p. 203°
Alcohol hydroxybenzoic acids ..	Orthohydroxymethylsalicylic (1 : 3 : 2), m. p. 142°	—
Aldehydo-hydroxybenzoic acids	Orthoaldehydosalicylic (1 : 3 : 2), m. p. 179°	Orthoaldehydometahydroxybenzoic acid (4 : 1 : 3), m. p. 234°
Hydroxyphthalic acids	β-Hydroxyisophthalic acid (1 : 3 : 4), m. p. 242°	Hydroxyterephthalic acid (1 : 4 : 3), m. p. above 300°

W. C. W.

Aurin. By R. S. Dale and C. Schorlemmer (*Chem. News*, **39**, 244).—The authors proved some time ago that when aurin, $C_{19}H_{14}O_3$, was heated with aqueous ammonia it was converted into pararosaniline ($C_{19}H_{17}N_3$). They assumed that this reaction took place in three dis-

tinct stages, the first being that in which 1 atom of oxygen in the aurin was replaced by HN from the NH_3; the second being where the second atom of oxygen left in the compound so formed was replaced by HN; and the third being the replacement of the third atom of oxygen from the second product by HN. They experimented with a view to obtain one of these intermediate products, and have succeeded in doing so. It is probably the one of the first stage. It occurs in beautiful crystals, dyes silk and wool a rich red, and they give to it the name *peonin*. It is formed by heating aurin with dilute ammonia at 100° C. for some weeks, but may also be produced by passing ammonia gas for a few hours into a solution of aurin in boiling amyl alcohol.

On heating aurin with methylamine for a few hours, trimethyl-pararosaniline was produced, according to the equation $C_{19}H_{14}O_3 + 3NH_2Me = C_{19}H_{14}Me_3N_3 + 3H_2O$. W. T.

Constitution of Sulphotoluide. By R. Otto (*Deut. Chem. Ges. Ber.*, **12**, 1175—1177).—Only one of the six possible modifications of this compound is known, and has been prepared in various ways by Deville (*Annalen*, **44**, 304); Otto and Grüber (*ibid.*, **154**, 193); Michael and Adair (*Ber.*, **10**, 583; **11**, 116); and lastly, by Beckurts and Otto (*ibid.*, **11**, 472, and 2066). The process employed by Michael and Adair, viz., the action of phosphoric anhydride on toluene- and paratoluenesulphonic acids, showed that the methyl-group of one toluene radicle was in the para-position as regards the SO_2 group. The position of the methyl group of the other toluene radicle was still uncertain, although it seemed probable that it was also in the para-position. This supposition is confirmed by the author, who has obtained the same sulphotoluide (m. p. 158°; b. p. = 405°; bar. = 714 mm.) by the oxidation of paratoluene sulphide $S(C_6H_4Me)_2$, in acetic acid solution, with the calculated quantity of potassium permanganate. It is therefore diparasulphotoluide, $C_6H_4Me.SO_2.C_6H_4Me$. The diparotoluenesulphide is best prepared as previously stated (*Annalen*, **149**, 101), by the dry distillation of the lead mercaptide of paratoluenesulphydrate. It crystallises in small white needles (m. p. 56° and not 42°, as given in a former communication; b. p. = 300° without decomposition), and is easily soluble in hot alcohol and benzene, and also in boiling glacial acetic acid and in ether, but is insoluble in water. T. C.

Fusion of Aromatic Acids with Soda. By L. Barth and J. Schreder (*Deut. Chem. Ges. Ber.*, **12**, 1255—1260).—By fusing aromatic acids with eight to ten times their weight of soda, the carboxyl group is first eliminated, and in some cases the products undergo further reactions.

Benzoic acid thus treated yields water and benzene—about 70—80 per cent. of the theoretical yield. A small quantity of diphenyl is formed, probably owing to the contact of the benzene vapours with the hot sides of the retort.

Trimellitic and hydrocinnamic acids yield the same products as benzoic acid. Cinnamic acid yields benzene chiefly (over 50 per cent.), and a small quantity of a high boiling oil, probably styrene.

Salicylic acid when heated at 340—355° is converted into phenol

(about 50 per cent.), which remains in combination with the alkali along with some unaltered salicylic acid. A better yield is obtained by heating it higher and conducting the operation more quickly.

Hydroxybenzoic acid is decomposed at 360°, and yields a smaller quantity of phenol, since a large proportion of the acid is completely oxidised. Parahydroxybenzoic acid yields similar results. In both these last two cases small quantities of salicylic acid were formed.

Protocatechuic acid is decomposed slowly between 330° and 350°, forming pyrocatechol, which contains some of the unaltered acid.

Dihydroxybenzoic acid decomposes a little above 350°, yielding 80—85 per cent. of the theoretical quantity of resorcinol, together with traces of condensation-products. From this it follows that this acid has a symmetrical constitution. In some experiments the formation of phloroglucinol was observed, which is doubtless formed from resorcinol (this vol., 633).

α-Dihydroxybenzoic acid prepared by Brunner from toluenedisulphonic acid, and probably identical with the 1 . 2 . 4 dihydroxybenzoic acid of Ascher, yields according to Senhofer at 286° as much as 60 per cent. of resorcinol. Its barium salt yields the same product when distilled with pumice stone.

Gallic acid is only partially and but slowly decomposed at 340°, pyrogallol and a small quantity of hexhydroxydiphenyl being formed. Owing to oxidation there is a considerable loss.

Phloretic acid requires a temperature above the boiling point of mercury, and at a certain stage yields parahydroxybenzoic acid, which by further fusion yields phenol.

Hydroparacoumaric acid is scarcely decomposed at 340°; if heated more strongly and for a short time, it is resolved into acetic and parahydroxybenzoic acids and phenol.

Paracoumaric acid is decomposed between 300° and 340°, yielding parahydroxybenzoic acid, which latter decomposes at higher temperature and yields phenol.

Hydroxyterephthalic acid is resolved at 340° into carbonic acid and a mixture of salicylic and hydroxybenzoic acids, which by further fusion yield phenol. P. P. B.

Aldehydhydroxybenzoic Acids from Metahydroxybenzoic Acid. By F. Tiemann and L. Landshoff (*Deut. Chem. Ges. Ber.*, **12**, 1334—1338).—The aldehydobenzoic acids obtained by the action of chloroform on alkaline solutions of salicylic and para-hydroxybenzoic acids have been previously described (*Ber.*, **9**, 1271).

Orthaldehydometahydroxybenzoic acid, $C_6H_3(OH)COH.COOH.[3:4:1]$, is best prepared by heating a solution of metahydroxybenzoic acid in soda with chloroform for five hours. After expelling the excess of chloroform, the mixture is acidified with hydrochloric acid, orthaldehydometahydroxybenzoic acid is precipitated, and the para-acid remains in the filtrate. The precipitate is dissolved in ether, and shaken up with a solution of hydrogen-sodium sulphite to separate the aldehydhydroxybenzoic acid from the unaltered metahydroxybenzoic acid. On the addition of sulphuric acid to the acid sodium sulphite double compound, the aldehydometahydroxybenzoic acid is precipitated.

To render the acid colourless, it is dissolved in hot water, and a small quantity of lead acetate and a few drops of ammonia are added to precipitate the colouring matter. The lead is removed by means of sulphuric acid. On cooling, the solution deposits white needle-shaped crystals, soluble in alcohol, ether, and in hot water. The crystals sinter when heated to 220°, and melt at 234°. The acid gives a yellow coloration with soda, and with ferric chloride a violet reaction. The neutral barium and calcium salts are easily soluble, the silver salt is crystalline. On oxidation with potassium permanganate, moist silver oxide, or by fusion with potash, orthaldehydometahydroxybenzoic acid yields hydroxyterephthalic acid, $C_6H_3.OH.COOH.COOH$ = [3:4:1].

The *paraldehydometahydroxybenzoic acid* is extracted with ether from the filtrate from which the ortho-acid has been precipitated. It can be separated from metahydroxybenzoic acid by means of hydrogen sodium sulphite, and also to a certain extent from orthaldehydohydroxybenzoic acid by its ready solubility in water. The para-acid has not yet been obtained in a state of purity. It appears to exist as an uncrystallisable syrup. Its silver salt is more soluble and less stable than the silver salt of the ortho-acid. W. C. W.

Iodosalicylic Acids. By H. Hübner (*Deut. Chem. Ges. Ber.*, **12**, 1347).—The *iodosalicylic* acid (m. p. 196°) derived from α-nitrosalicylic acid (m. p. 228°) forms the following salts—

$$C_6H_3I(OH)COONa.H_2O;\ [C_6H_3I(OH).COO]_2Mg + 6H_2O,$$

and $[C_6H_3I(OH)COO]_2Ca + 6H_2O$, crystallising in colourless prisms. $[C_6H_3I(OH)COO]_2Ba + 4H_2O$, forming colourless plates. The *lead* salt is obtained as a white, and the *silver* salt as a yellow precipitate. Meta-iodonitrosalicylic acid (m. p. 204°) is obtained when this acid is nitrated. W. C. W.

Nitrosalicylic Acids and Dinitrophenols. By H. Hübner, S. M. Babcock, and H. Schaumann (*Deut. Chem. Ges. Ber.*, **12**, 1345—1347).—The authors have shown the relative position of the nitro-groups in dinitrosalicylic acid by converting the acid into dinitrophenol, dinitraniline, and metadinitrobenzene (m. p. 89—90°). From dimetanitrosalicylic acid, α-nitramidosalicylic acid—

$$COOH : OH : NH_2 : NO_2 = [1 : 2 : 3 : 5],$$

and α-nitrosalicylic acid (m. p. 228°) were obtained. By nitrating β-nitrosalicylic acid, β-dinitrophenol, $OH : NO_2 : NO_2 = [1 : 2 : 6]$ (m. p. 63°), is produced, whilst α-dinitrophenol, $OH : NO_2 : NO_2 = [1 : 2 : 4]$ (m. p. 114°), is formed by the decomposition of dimetanitrosalicylic acid. W. C. W.

Parahydroxysalicylic Acid. By A. Goldberg (*J. pr. Chem.* [2], **19**, 359—381).—The object of this investigation was to determine the constitution of hydroxysalicylic acid prepared from diazosalicylic acid (R. Schmitt, *Zeits. Chem.*, 1864, p. 321) by comparison with the acids previously described by Liechti, Demole, and others (*Annalen*, *Suppl.*, **7**, 129; *Ber.*, **7**, 1436, &c.).

Respecting the preparation of the diazo-acid, it is remarkable that

the action of nitrous acid on amidosalicylic acid, dissolved in excess of aqueous hydrochloric acid, gives rise, in addition, to tri- and tetrachloroquinone. The minimum yield of secondary products is attained by passing nitrous anhydride in large excess into the well-cooled alcoholic solution of the amido-acid. In this case the sole bye-product is paranitrosalicylic acid, formed probably according to the equation :—

$$C_6H_3(COOH)<_{N=N}^{O}> + HNO_2 = C_6H_3(OH)(NO_2).COOH + N_2.$$

On passing nitrous anhydride into the ethereal solution of salicylic acid, a certain quantity of paradiazosalicylic acid is formed, but the chief product of the reaction is paramononitrosalicylic acid, the comparative yield of the latter being about 20 : 1 (*Ber.*, **8**, 98). The formation of the latter is here also probably referable to the secondary decomposition of the diazo-acid. The diazo-acid was converted into iodosalicylic acid by the action of warm hydriodic acid. The homogeneity of the product was established by the constant melting point (196°) observed in each of four successive crystallisations. It is therefore identical with the acid described by Lautemann (*Annalen*, **120**, 311) and with one of the isomerides obtained by W. Fischer (*ibid.*, **180**, 347) by the direct action of iodine on salicylic acid, but distinct from that described by Liechti and Demole (*loc. cit.*).

The iodo-acid was converted into hydroxysalicylic acid by fusion with alkali; this acid was obtained mixed with a bye-product (subsequently proved to be an ethereal anhydride), from which it was separated by precipitating the aqueous solution of the mixture with neutral lead acetate. Hydroxysalicylic acid, melting constantly at 196—197°, was isolated from the filtrate. It crystallises in well-formed needles, which are easily soluble in water, alcohol, and ether; less soluble in dilute mineral acids, in contact with which the acid develops a brown colour. The aqueous solution gives a deep blue colour with ferric chloride; it reduces Fehling's solution and silver nitrate, the latter in the cold. On dry distillation, the acid yields hydroquinone. The acid is dissolved by ammonia, with but slight coloration, but a red-brown colour is speedily developed. The ethyl salt is prepared by heating the alcoholic solution of the acid with a few drops of sulphuric acid for 20—24 hours on the water-bath 100°. It is precipitated on adding water, and on recrystallising from the hot aqueous solution is obtained in colourless needles (m. p. 75°). It has a pleasant fruity odour; it volatilises with steam.

The direct conversion of the diazo-acid into hydroxysalicylic acid by boiling it with water is attended with the formation of resinous bye-products (yielding hydroxysalicylic acid on boiling with dilute mineral acids, and therefore probably anhydrides) in large quantity. By previously adding sufficient sulphuric acid to unite with the diazo-compound, the yield of hydroxysalicylic acid is largely increased. The product is identical with that of the previous reaction. This is sufficient proof that the OH-groups of this hydroxysalicylic acid occupy the para-position. C. F. C.

Phenolglycollic Acids. By P. Giacosa (*J. pr. Chem.*, [2], **19**,

396—399).—Heintz first prepared phenolglycollic acid (*Pogg. Ann.*, **109**, 489) by heating together monochloracetic acid and sodium-phenol for some time at 150°, but this process may be advantageously modified as follows:—Phenol and monochloracetic acid in equivalent quantities are melted together on the water-bath; aqueous sodium hydrate (sp. gr. 1·3) is then added, slowly and with continuous stirring, in quantity about four times that of the phenol employed. The reaction is rapidly completed, and the liquid solidifies on cooling to a crystalline mass of the sodium salt. Nearly pure phenolglycollic acid is obtained from the sodium salt after it has been drained by means of the filter pump, by decomposing it with dilute hydrochloric acid. The method appears to admit of general application; thus pyrogallol (1 mol.) reacts with sodium monochloracetate (3 mols.) to form the triglycollic acid, $C_6H_3(OCH_2.COONa)_3$. This acid crystallises from aqueous solution in long colourless needles (m. p. 198°). The normal potassium salt is precipitated by alcohol from its aqueous solution in white needles. On adding acetic acid to the solution of the above salt a slightly soluble acid salt, $C_{12}H_{11}O_9K.H_2O$, is precipitated.

C. F. C.

Ellagic Acid. By L. Barth and G. Goldschmidt (*Deut. Chem. Ges. Ber.*, **12**, 1237—1255).—The ellagic acid used in this investigation was prepared from divi-divi by a method given in a former communication (*Wien Akad. Ber.*, **77**, 2 Abth., 1878). The formulæ $C_{14}H_6O_8 + 2H_2O$ and $C_{14}H_8O_9 + H_2O$ have been proposed for this acid, Merklein and Wohler (*Annalen*, **55**, 133) and Remhold (*ibid.*, **193**, 285) advocating the former, whilst the latter is supported by Schiff (*ibid.*, **170**, 43). The authors have made a series of water determinations at different temperatures, and have obtained numbers corresponding with the formula $C_{14}H_6O_8 + 2H_2O$. The acid loses scarcely any water below 100°; when dried at 110° and then placed in a vessel over water it takes up 9 per cent. of water very quickly; the absorption of the rest takes place very slowly. The acid dried at 210° takes up water under the same circumstances, but very slowly. Further the acid dried above 100° begins to lose weight only at such temperatures that a partial decomposition takes place. Finally the acid dried at 120° gives on combustion numbers corresponding with the formula $C_{14}H_6O_8$.

The numbers obtained by analysis of the sodium salt prepared by two methods, first, that of Wöhler and Merklein (*loc. cit.*); secondly, that of Ernst and Zwenger (*Annalen*, **159**, 27), agree more nearly with the formula $C_{14}H_4Na_2O_8$ than $C_{14}H_6Na_2O_9$. Finally the acetyl-derivative prepared by Liebermann's method (*Ber.*, **11**, 1618) has a percentage composition which can only be derived from the formula $C_{14}H_6O_8$. The authors have sought to determine the acetyl groups present by boiling the compound with baryta-water, then precipitating the unused baryta by carbonic acid, and determining the amount of barium acetate by means of sulphuric acid. The results so obtained show the derivative to contain five acetyl groups.

Ellagic acid heated with lime or soda lime in a current of hydrogen is almost entirely carbonised, a small portion passing over undecomposed.

	a.	*β.*	*γ.*
Crystalline form....	Well-formed leaflets, having a silver lustre, sometimes united in form of rosette, sometimes united so as to look like silver foil	Colourless, small needles.....	Shining, colourless needles, often of considerable size, easily turning grey.
Melting point.....	——	Undetermined, blackens at 250°	Undetermined, blackens at 230°.
Solubility	Not very soluble in water, easily in alcohol	Sparingly soluble in cold, easily in hot water. Sparingly soluble in cold, but more easily in hot alcohol. Sparingly in boiling ether, benzene, carbon bisulphide, and chloroform	More sparingly soluble in water than *β*. Easily soluble in alcohol, sparingly in ether, benzene, carbon bisulphide, and chloroform.
With caustic potash	Beautiful bluish-violet, unstable, passing into brown	Beautiful bluish-violet, unstable, passing to blood-red, then brown	Blood-red, passing to brown, to fine emerald green, finally yellow.
Ferric chloride	Bluish-grey precipitate ..	Intense yellowish-brown coloration, fading, and on addition of a little soda becoming blue, and violet on adding more; after standing, cherry-red. Soda produces a brown precipitate in presence of large quantity of ferric chloride	Green, which fades, soda gives a blue-violet, on further addition a red-violet, changing to brown on standing. In presence of large quantity of ferric chloride soda gives blackish-brown flocks.
Ferrous salts	——	Blue coloration, darker on standing	Same as *β*.
Lead acetate	A green precipitate, quickly changing to black	White precipitate, changing to blue, bluish-grey and dark	Dirty-brown precipitate.
Copper acetate	A reddish coloration, quickly turning blue, slow separation of blue precipitate	Reddish-brown flocculent precipitate	Dirty-blue precipitate.
Acetyl derivatives ..	Colourless, prismatic crystals, m. p. 145°	White, hard, large prisms, m. p. 170°	——

When heated with concentrated hydriodic acid or hydriodic acid and amorphous phosphorus, ellagic acid is converted into the anhydrous acid $C_{14}H_6O_8$, which is obtained as a yellow, shining, crystalline substance. Concentrated hydrochloric acid has the same effect; the product is, however, of a darker colour, the higher the temperature to which the mixture is heated.

By fusion with potash, ellagic acid yields a hexoxydiphenyl, isomeric with the α-hexhydroxydiphenyl prepared by Liebermann (*Annalen*, **169**, 221) from hydrocörulignone. This body, β-hexhydroxydiphenyl, crystallises from water in colourless needles; when distilled with zinc-dust in a current of hydrogen it yields diphenyl. When caustic soda is substituted for potash, besides β-hexhydroxydiphenyl a third isomeride of α-hexhydroxydiphenyl is formed; this may be called γ-hexoxydiphenyl. The two are separated by the difference of solubility in cold water, the γ-derivative being almost insoluble. By recrystallisation from hot water it is obtained in shining colourless needles, often of considerable length, which become grey on exposure to the air.

The table (p. 931) contains the results of a comparative study of these three isomerides.

By acting upon ellagic acid with a boiling solution of potash, the intermediate product of the reaction is formed. It is obtained as a crystalline mass by distilling the ether extract, and on crystallisation from boiling water is obtained in microscopic needle-shaped prisms of the composition of hexhydroxydiphenyl ketone, $C_{13}H_8O_7$, and that it is this compound is proved by its yielding fluorene when distilled with zinc-dust.

Hexhydroxydiphenyl ketone melts at a very high temperature, and blackens at 250°. It is sparingly soluble in hot water, largely soluble in alcohol, and but sparingly in ether, benzene, chloroform, and carbon bisulphide. Its aqueous solutions give with a trace of caustic alkali a yellowish-brown coloration, which on shaking becomes dark yellowish-red and finally carmine; when diluted, it turns yellow. An alcoholic solution treated with an alkali gives a green precipitate, or becomes of a carmine colour on adding water.

Ferric chloride produces in dilute solutions a bluish-green coloration; in concentrated solutions, a bluish-black precipitate is formed. Soda added to these solutions gives according to their concentration a red or brown coloration or a brown precipitate.

Ferrous salts gives the same reaction as with pyrogallic acid. Lead acetate gives a bright green flocculent precipitate, which becomes darker; copper acetate a dark green coloration. The ketone gives with carbonate of soda the same reaction as with caustic soda; carbonic acid is also evolved.

Of the two possible constitutional formulæ corresponding with $C_{14}H_6O_8$

for ellagic acid, $C_6H(OH)_3\langle\begin{matrix}CO\\ \\ \end{matrix}\rangle C_6(OH)_2\langle\begin{matrix}O\\ CO\end{matrix}\rangle$ I

and $C_6H(OH)_2\langle\begin{matrix}CO\\ O\end{matrix}\rangle C_6(OH)_2COOH$ II,

the authors prefer I, for in no case does ellagic acid appear to possess

the characters of an aromatic acid, and further, this formula accounts for the formation of an acetyl-derivative containing five acetyl groups. Further, the formation of hexhydroxydiphenyl-ketone and hexhydroxydiphenyl is also easily explained. Hence ellagic acid may be styled hexhydroxydiphenyl-ketone-carbonic anhydride.

P. P. B.

Antimony Tannate. By Ellen S. Richards and Alice W. Palmer (*Am. J. Sci.* [3], **16**, 196 and 361).—From analyses of antimony tannate from purified tannin, the authors deduce the formula $Sb_2(C_{14}H_8O_9)_3 + 6H_2O$, in which tannin is considered as digallic acid with possibly three atoms of typical hydrogen replaced by antimony, as well as the three basic hydrogen atoms.

The authors describe some modifications of Gerland's process for tannin estimation which they have been led to adopt, and confirm his statement that gallic acid does not affect the results. They find, however, that the presence of colouring matter in the extract vitiates the results by combining with antimony. This is particularly the case with sweet fern leaves and hemlock bark. The sweet fern contains a yellow colouring matter allied to quercetin. C. W. W.

Preparation of Sulpho-compounds from Diazo-compounds by means of Sulphurous Acid. By F. H. S. Müller and F. Wiesinger (*Deut. Chem. Ger. Ber.*, **12**, 1348—1349).—The authors have prepared toluene-, ortho-, meta-, and para-sulphonic acids by the action of sulphurous acid on the diazo-compounds. W. C. W.

Derivatives of α-Phenoldisulphonic Acid. By L. Barth and M. v. Schmidt (*Deut. Chem. Ges. Ber.*, **12**, 1260—1267).—Potassium α-phenoldisulphate when fused with potash yields α-dihydroxybenzenesulphonic acid, $C_6H_3(OH)_2.SO_3H$, which is obtained in needle-shaped crystals by allowing its aqueous solution to evaporate slowly. Its aqueous solutions have a strongly acid reaction, and give with ferric chloride an intense green coloration, which becomes successively blue, violet, and red on the addition of sodium carbonate. Lead acetate gives no precipitate with the aqueous solutions of the acid or its salts, but basic lead acetate gives a white precipitate.

The potassium salt, $C_6H_3(OH)_2.SO_3K$, is easily soluble in water, and sparingy in absolute alcohol. The sodium salt, $C_6H_3(OH)_2.SO_3Na + H_2O$, crystallises in colourless prisms. The barium salt,

$$[C_6H_3(OH)_2.SO_3]_2Ba,$$

is easily soluble in water, and crystallises from alcohol in needles united in concentric masses. Dihydroxybenzenesulphonic acid when fused with potash yields no trioxy-derivative.

Sodium α-phenoldisulphonate when fused with soda is partly burnt, protocatechuic acid, pyrocatechol, and some of the above monosulpho-derivatives being formed, together with other products which form a syrupy mass.

The authors have found that when pure protocatechuic acid is converted into the barium salt by boiling its aqueous solution with barium carbonate, and the solution of the salt is then shaken up with ether, as

much as 22·4 per cent. of the acid may be extracted. This is probably due to the formation of basic salts.

Dihydroxybenzenesulphonic acid when fused with soda yields the same products as α-diphenoldisulphonic acid. The formation of pyrocatechol shows this dihydroxybenzenesulphonic acid to be a pyrocatecholsulphonic acid or protocatechuic acid, in which the carboxyl group is replaced by the sulphoxyl group. This conclusion is supported by the colour reactions this sulphonic acid gives with ferric chloride, and which resemble those of protocatechuic acid.

P. P. B.

Resorcinol-disulphonic Acid. By V. Tedeschi (*Deut. Chem. Ges. Ber.*, **12**, 1267—1271).—By treating resorcinol with sulphuric acid Piccard and Humbert obtained a disulphonic acid which forms a very sparingly soluble basic barium salt. By treating resorcinol with a mixture of one part of sulphuric acid and two of sulphuric anhydride, the author has obtained a disulphonic acid which crystallises in white silky needles having the composition $C_6H_2(HSO_3)_2(OH)_2 + 2H_2O$. When heated at 100°, or when its aqueous solution is boiled, it is decomposed.

The potassium salt, $C_6H_2(KSO_3)_2(OH)_2 + H_2O$, crystallises in broad prismatic needles, easily soluble in water but insoluble in alcohol. Its aqueous solution and that of the acid give a red coloration with ferric chloride. The neutral barium salt, $C_6H_2(OH)_2 \cdot S_2O_6Ba + 3H_2O$, crystallises in colourless needles, and is obtained by saturating the free acid with barium carbonate and evaporating the filtrate. It is easily soluble in water. Its solution when treated with barium carbonate, filtered, and boiled, gives a slight crystalline precipitate of a basic salt. The pure crystalline acid when converted into the barium salt and treated in the same way exhibits this separation of basic salt to a greater extent, the solution becoming acid. In this it agrees with the acid prepared by Piccard and Humbert, and a comparison of the crystalline form of the potassium salts shows the acids to be identical.

The author has also prepared the calcium and sodium salts, which are both well crystallised compounds.

This resorcinoldisulphonic acid fused with potash yields phloroglucinol and small quantities of other products. Fusion with soda yields less favourable results.

P. P. B.

Polysubstituted Carbamides. By W. Michler and C. Exherich (*Deut. Chem. Ges. Ber.*, **12**, 1162—1164).—*Chloride of dimethylcarbamide*, $Cl.CO.NMe_2$, is obtained by saturating well-cooled anhydrous benzene with carbonic chloride, and treating the solution thus obtained with dimethylamine. It is a transparent colourless liquid (b. p. 165°) of peculiar odour, and is easily soluble in benzene, ether, and carbon bisulphide. It is gradually decomposed by water into hydrochloric acid, dimethylamine, and carbonic anhydride. It is readily acted on by ammonia, aniline, &c.

Phenyldimethylcarbamide, $Me_2N.CO.NHPh$, is best prepared by dissolving aniline in 10—15 vols. of benzene, and adding to the solution an equivalent quantity of the chloride of dimethylcarbamide. It separates from alcohol in white crystals, which are easily soluble in

alcohol, ether, and benzene. If concentrated solutions are used in the preparation of this compound, a different decomposition takes place, and carbanilide is frequently obtained.

Tetramethylcarbamide, $CO(NMe_2)_2$, is obtained by dissolving the chloride of dimethylcarbamide in an equal volume of anhydrous benzene, and passing dimethylamine into the solution. It is a colourless transparent liquid (b. p. 176°), which is easily soluble in alcohol and ether. Vapour-density = 3·934, calculated = 4·012. T. C.

Polysubstituted Carbamides. By W. Michler and R. Zimmermann (*Deut. Chem. Ges. Ber.*, **12**, 1165—1167).—*Chloride of Methylphenyl-carbamide*, Cl.CO.NMePh, is obtained by dissolving monomethylaniline (b. p. 193°) in benzene, and treating the solution thus obtained with carbonic chloride. It crystallises in rhombic tables (m. p. 88°, b. p. 280°), which are insoluble in water, but easily soluble in alcohol and ether.

Diphenyl-dimethylcarbamide, $CO(NMePh)_2$, is prepared by the action of alcoholic ammonia or of monomethylaniline and zinc-dust on the above compound. It forms monosymmetric crystals (m. p. 120°, b. p. 350°), which are easily soluble in alcohol, ether, and benzene, but insoluble in water.

Tetraphenylcarbamide may also be obtained by a method analogous to that employed in the case of the last compound, viz., by heating diphenylamine with the chloride of diphenylcarbamide in the presence of zinc-dust. T. C.

Tolylthiocarbimide. By G. Lachmann (*Deut. Chem. Ges. Ber.*, **12**, 1349—1350).—By the action of chlorine on orthotolylthiocarbimide which has been diluted with chloroform, the dichloride $C_6H_4Me.CNCl_2$ (b.p. 218°) is formed. This substance is insoluble in water; it is decomposed by alcohol and by glacial acetic acid. When treated with alcoholic potash it splits up, yielding a beautifully crystalline urethane—

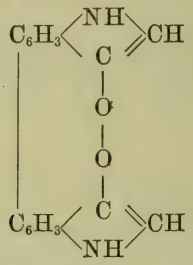
$$EtO.CO.NH.C_6H_4Me,$$

and ortho-ditolylcarbamide $CO(NH.C_6H_4Me)_2$. The urethane can also be prepared by the action of sodium alcoholate on the chloride. It melts at 46°, and dissolves in alcohol, benzene, and petroleum. The carbamide is obtained by the action of water at 100° on the chloride. This compound crystallises in silky needles (m. p. 250°), which are sparingly soluble in alcohol and benzene. W. C. W.

Constitution of Indigo. By E. Baumann and F. Tiemann (*Deut. Chem. Ges. Ber.*, **12**, 1192—1195).—In a recent communication (*Ber.*, **12**, 1098) the authors proposed a constitution for indigo, according to which it is a diphenyl-quinone in which the group C_2H_3N is contained twice. In confirmation of this view they have made further investigations, especially as regards the relation of indoxyl to the decomposition products of indigo. Under certain conditions indigo yields tribromphenol and tribromaniline, but if indoxyl has the constitution generally ascribed to it, viz., $OH.C_6H_3\begin{matrix}CH\\ \diagup\!\!\diagdown\\ NH\end{matrix}\!\!>CH$, it could not give directly

a body having the composition of tribromaniline, and yet experiment has shown that it does yield a tribromaniline (m. p. 119°). Consequently the phenol nature of indoxyl is inadmissible, it being more probable that the OH group is not attached to the benzene nucleus but to the side-chain. This supposition is proved by the fact that heated potassium indoxyl sulphate when heated with dry barium hydroxide, gives only aniline and neither amido-phenol nor oxyanthranilic acid; further, the same substance, on oxidation with potassium permanganate in dilute aqueous solution, gives anthranilic acid.

Isatin chloride, $C_6H_4\begin{<}{CO}{N}\end{>}CCl$, has been converted by Baeyer (*Ber.*, **11**, 1296; **12**, 456) into indigo by reduction with zinc-dust in acetic acid solution and subsequent exposure to the air. In this reaction, it is probable that indoxyl is first produced, and afterwards converted by the oxygen of the air into indigo, from which it would follow that indoxyl is $C_6H_4\begin{<}{C(OH)}{NH}\end{>}CH$, and that indigo itself is probably—



This formula readily explains the analogy in composition of indigo and cedriret, the quinone nature of indigo, and the formation of aniline and anthranilic acid therefrom. It is, however, not decided whether the two indoxyl groups are united by the two benzene nuclei ($C_6H_5.C_6H_5$) or by the side-chains ($C_6H_5.C_2H_2.C_2H_2.C_6H_5$). T. C.

Derivatives of Indigotin. By E. Giraud (*Compt. rend.*, **89**, 104).—By heating white indigo with a concentrated solution of sodium thiosulphate made alkaline with soda, at 175—180° for 48 hours, a dark brown solution is obtained, which on exposure to the air becomes green, and forms a red deposit. This, when extracted with alcohol, leaves a residue of indigotin, and the alcoholic solution on evaporation yields a dark-red body, having the composition $C_{32}H_{22}N_4O_4$. This dissolves in caustic alkalis with a green colour, which changes to yellow on boiling, due to the formation of a body having acid properties, and a yellow colouring matter $C_{32}H_{24}N_4O_5$. The sodium salt has the composition $C_{32}H_{24}Na_2O_5$(?). This acid, when heated with zinc-dust, forms indoline, $C_{16}H_{14}N_2$, which can be obtained directly from indigotin by heating it with sodium thiosulphate and an excess of caustic soda. It appears to be identical with the flavindin of Laurent. L. T. O'S.

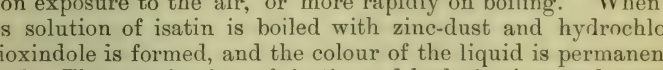
Isatin Derivatives. By W. Suida (*Deut. Chem. Ges. Ber.*, **12**, 1326—1328).—*Acetyldioxindole*, $C_{10}H_9NO_3$, prepared by the action of acetic anhydride on dioxindole at 140°, is deposited from an aqueous solution in colourless prisms (m. p. 127°), which are soluble in alcohol, ether, benzene, and hot water.

Acetylhydrindic acid can be obtained by dissolving acetyldioxindole in cold baryta-water, and precipitating the barium with dilute sulphuric acid. The acid is extracted from the filtrate by means of ether.

Acetoxindole, $C_{10}H_9NO_2$, obtained by boiling oxindole with an excess of acetic anhydride for 4 or 5 hours, forms long, colourless needle-shaped crystals (m. p. 126°), which dissolve in ether, alcohol, and hot water. By the action of soda solution, acetoxindole appears to be converted into acetyl-orthamidophenyl-acetic acid.

W. C. W.

The Indigo-blue Group. By A. Baeyer (*Deut. Chem. Ges. Ber.*, **12**, 1309—1319).—I. *Isatin.*—A solution of isatin in glacial acetic acid, or an alcoholic solution of isatin which has been acidified by acetic or hydrochloric acid, becomes colourless when treated with zinc-dust. This is due to the formation of hydroisatin. The liquid regains its orignal colour on exposure to the air, or more rapidly on boiling. When an aqueous solution of isatin is boiled with zinc-dust and hydrochloric acid, dioxindole is formed, and the colour of the liquid is permanently destroyed. The constitution of isatin and hydroisatin may be represented thus :—



Isatin. Hydroisatin.

Isatin combines with tertiary bases, phenols, and hydrocarbons to form condensation-products. When a mixture of isatin and phenol is gently warmed with concentrated hydrochloric acid, a white compound is formed, which separates out on the addition of water.

Indophenin, $C_{20}H_{15}NO$, is prepared by shaking together a solution of isatin in 30 parts of strong sulphuric acid with pure benzene until a pure blue colour is produced. The mixture is poured into water, filtered, and washed with dilute soda, and is afterwards boiled with water, glacial acetic acid, alcohol, and finally with ether,

$$C_8H_5NO_2 + 2C_6H_6 = C_{20}H_{15}NO + H_2O.$$

In a similar way compounds of toluene, xylene, and naphthalene with isatin may be prepared. They do not, however, possess the characteristic colour of indophenin.

The blue colour of this compound is so intense that this reaction may be used as a test for isatin or benzene : $\frac{1}{2000}$ milligram of isatin gives a decided greenish-blue coloration when warmed with sulphuric acid and benzene.

Indophenin strongly resembles indigo blue in appearance. It is sparingly soluble in alcohol, ether, chloroform, and glacial acetic acid. It dissolves freely in concentrated sulphuric acid and in phenol, and is precipitated from the solutions on addition of water or alcohol.

By the action of reducing agents, colourless solutions are obtained, which turn blue on exposure to the air.

Bromindophenin, $C_{20}H_{14}NOBr$, resembles the preceding compound in its properties. It is prepared by warming a mixture of bromisatin, benzene, and strong sulphuric acid.

Nitroisatin, $C_8H_4(NO_2)NO_2$, is prepared by adding potassium nitrate to a solution of isatin in sulphuric acid, which is cooled down in a freezing mixture. The product of the reaction is poured upon ice, and the nitroisatin which separates out is recrystallised from alcohol. In this way it is obtained in small pink needles, which melt at 226—230°, and decompose at a higher temperature. The crystals are soluble in alcohol; they also dissolve in potash, forming a reddish-yellow solution from which the potassium salt is slowly deposited.

II. *Oxindole and Indole.—Nitroxindole*, $C_8H_6(NO_2)NO$, prepared in the same way as nitroisatin, crystallises in yellow needles, which are soluble in warm alcohol, and dissolve in potash, producing a reddish-yellow solution. Nitroxindole begins to decompose at 175°, forming a white sublimate.

Retinindole, C_8H_8NO or C_8H_9NO, is prepared by adding a concentrated solution of hydriodic acid in glacial acetic acid to oxindole chloride dissolved in acetic acid. Sulphurous acid is added to the dark-coloured liquid; the mixture is then filtered, and the retinindole is thrown down as a yellowish-white precipitate by soda.

Acetylindole, $C_8H_6N.Ac$, formed by the action of acetic anhydride on indole at 180—200°, can be obtained in colourless needles by recrystallisation from benzene and from water. It melts at 182°, and sublimes without decomposition.

III. *Indigo-blue Substitution-products.—Bromisatin chloride*—

$$C_8H_3NOBrCl,$$

prepared by boiling a mixture of monobromisatin, benzene, and phosphorus pentachloride, crystallises in glistening needles of a reddish-brown colour. It dissolves freely in hot benzene, alcohol, ether, and chloroform.

Bromindigo, $C_{16}H_8Br_2N_2O_2$, is prepared by boiling bromisatin with a mixture of phosphorus pentachloride and phosphorus oxychloride, and pouring the product into an excess of a 10 per cent. solution of hydriodic acid in glacial acetic acid. On the addition of aqueous sulphurous acid and water, bromindigo and a small quantity of bromindigopurpurin separate out. Bromindigo dissolves in strong sulphuric acid, forming a green solution, which turns blue when heated. The solution in phenol deposits compact black crystals on the addition of a small quantity of alcohol. Bromindigo sublimes when heated, forming purple vapours. Bromindigopurpurin is deposited from a mixture of ether and alcohol in dark needles.

Nitroindigo, $C_{16}H_8(NO_2)_2N_2O_2$.—Nitroisatin is boiled with a mixture of phosphorus oxychloride and pentachloride until it is completely dissolved. The liquid is cooled down in a freezing mixture, and mixed with a solution of hydriodic acid in glacial acetic acid. The nitroindigo separates out as a reddish-violet precipitate when the product of this reaction is poured into a mixture of dilute sulphurous acid and ice.

Nitroindigo forms a dark cherry-red powder, soluble in nitrobenzene, phenol, and in strong sulphuric acid. It detonates when heated.

Nitroindigopurpurin, which is formed in small quantities, may be obtained by exhausting the crude nitroindigo with boiling alcohol.

Amidoindigo, $C_{16}H_8(NH_2)_2N_2O_2$, is prepared by boiling finely-powdered nitroindigo with acetic acid and zinc-dust until a colourless liquid is obtained. The solution is filtered and neutralised with soda, when the amidoindigo separates out as a blue flocculent precipitate. To free the crude product from zinc, the precipitate is dissolved in hydrochloric acid, the solution neutralised with soda, and the amidoindigo precipitated by sodium acetate. This substance is soluble in dilute mineral acids and in glacial acetic acid, forming a blue solution. It is charred by the action of heat. W. C. W.

Orthodiamidodiphenethole (Diethoxybenzidine). By Möhlau (*J. pr. Chem.* [2], **19**, 381—393).—The salts of the above base are formed by the action of acids on hydrazophenethole, the reaction being strictly analogous to the typical decomposition of the hydrazo-derivatives of the hydrocarbons, thus:—

$$\begin{matrix} C_6H_4(OEt).NH \\ | \\ C_6H_4(OEt).NH \end{matrix} + H_2SO_4 = \begin{matrix} C_6H_4(OEt).NH_3O \\ | \\ C_6H_4(OEt)NH_3O \end{matrix} \rangle SO_2.$$

They are distinguished from the corresponding salts of orthamidophenethole, with which they are isomeric, by yielding a white amorphous precipitate of the base on the addition of an alkali, whereas the other base is separated as a yellowish oil. In the pure state, in which it is best obtained through the medium of the double compound of the chloride with stannous chloride, it crystallises in colourless needles (m. p. 117°), which are easily soluble in alcohol, ether, and chloroform, to a certain extent in boiling water, but almost insoluble in the cold. At a high temperature it distils with partial decomposition. Under the action of oxidising agents it exhibits phenomena similar to those described by Schulz for benzidine (*Annalen*, **174**, 226). On agitating the ethereal solution with traces of bromine, a beautiful moss-green colour is developed, which changes to brown on standing. The base is decomposed by concentrated hydriodic acid at 120°, with formation of ethyl iodide and a crystalline body, the iodide either of orthodehydroxydiamidodiphenyl or of diamidodiphenyl.

The following details are given respecting its salts:—The *hydrochloride* crystallises in prismatic tables or in long slender needles, which are soluble in water, somewhat soluble in alcohol, insoluble in ether. It withstands a temperature of 120° without change, but cannot be fused without decomposition. In aqueous solution, it acts as a powerful reducing agent, separating gold, silver, and platinum from solutions of their salts. With ferric chloride, as with other oxidising agents, it developes a deep red colour. Its double compound with stannous chloride crystallises in rhombic plates, which are easily soluble in water, somewhat soluble in alcohol, but insoluble in ether. The platinochloride is obtained by adding platinum chloride, dissolved in concentrated hydrochloric acid, to the alcoholic solution of the salt,

no reduction occurring under these circumstances. It crystallises with 3 mol. H_2O in transparent microscopic prisms, which are insoluble in alcohol and in ether. The *sulphate* crystallises in shining needles, which are soluble in water and dilute alcohol, but insoluble in ether. The *nitrate* crystallises in colourless needles. It cannot be prepared in the pure state, in the same manner as the sulphate and chloride, by the action of the acid upon hydrazophenethole, but is obtained by adding nitric acid to the alcoholic solution of diamidodiphenethole and allowing it to evaporate spontaneously.

C. F. C.

Preparation of Hexamethylbenzene from Acetone. By H. Greene (*J. pr. Chem.* [2], **19**, 336.—When acetone is heated to a high temperature with zinc chloride, various olefines and considerable quantities of hexamethylbenzene are produced, but no trace of mesitylene.

M. M. P. M.

Action of Phthalic Anhydride on Naphthalene in presence of Aluminium Chloride. By E. Ador and J. M. Crafts (*Compt. rend.*, **88**, 1355—1358).—To a mixture of 500 grams of naphthalene and 200 of phthalic anhydride, heated to 100°, 250 grams aluminium chloride were added; hydrochloric acid was evolved, and at the end of six hours the mass was extracted with hot water, which dissolved out about 50 grams phthalic acid, leaving a black residue. This was treated several times with dilute soda, and the solution fractionally precipitated with an acid. By this means 2 grams of an acid were obtained crystallising from dilute alcohol in small white prisms (m. p. 173·5°); from strong alcohol it crystallises in rosettes consisting of long needles, and the mother-liquor deposited prisms having the same melting point. The results of analysis correspond with those required for orthonaphthoylbenzoic acid, $C_{10}H_7.CO.C_6H_4.COOH$. The barium salt crystallises from alcohol in needles, is very hygroscopic, and dissolves readily in water and in alcohol; it melts at 160°.

The first fractions of the precipitate of orthonaphthoylbenzoic acid form black resinous masses which totally decompose on distillation.

The residue left on treatment of the original product with soda when extracted with alcohol to remove naphthalene, and distilled, loses water, and at 300° a thick liquid comes over; if this is dissolved in benzene and alcohol added to the solution, it deposits yellow plates on standing, and the mother-liquors have a green fluorescence. These plates recrystallised from a mixture of alcohol and ether, melt at 181—186°. The results of analysis agree with those of pyrene or chrysene. It does not, however, give the reactions for these bodies; it forms a resinous nitro-derivative and a crystalline bromo-compound, melting at 112°. This body is a secondary product.

From a second experiment, in which 500 grams of naphthalene were slowly added to a mixture of 250 of aluminium chloride, and 200 grams phthalic anhydride, no results were obtained.

Since naphthalene and phthalic anhydride are bodies entering into the reaction, the hydrocarbon may be supposed to contain the 10 atoms of carbon of naphthalene and the 8 atoms of phthalic anhydride, and to have the empirical formula $C_{18}H_{12}$, and thus be isomeric with chrysene.

L. T. O'S.

Nitrophenanthrene and its Derivatives. By G. A. Schmidt (*Deut. Chem. Ges. Ber.*, **12**, 1153—1160).—Three isomeric nitrophenanthrenes are obtained when nitric acid (sp. gr. 1·35) is allowed to act slowly on phenanthrene mixed with sand. They are separated with great difficulty by fractional crystallisation from alcohol, ether, toluene, and glacial acetic acid.

α-Mononitrophenanthrene, $C_{14}H_9(NO_2)$, is obtained in largest quantity, and is identical with the mononitrophenanthrene described by Graebe (*Annalen*, **167**, 155). It crystallises from alcohol or glacial acetic acid in straw-yellow needles (m. p. 74°; Graebe, 70—80°). The presence of small traces of impurities causes it to remain liquid even at very low temperatures. By reduction with tin and hydrochloric acid, or alcoholic ammonium sulphide, *α-amidophenanthrene hydrochloride*, $C_{14}H_9(NH_2).HCl$, is obtained as a white crystalline precipitate, which is sparingly soluble in water, and is rapidly decomposed on exposure to the air. The *sulphate*, $(C_{14}H_9.NH_2)_2H_2SO_4$, is much more stable, and consists of a white powder sparingly soluble in alcohol and in water.

α-Amidophenanthrene is insoluble in water, and crystallises from dilute alcohol in small yellow plates.

α-Mononitrophenanthrenequinone is formed by the oxidation of the nitro-compound with chromic and acetic acids. It crystallises in brilliant orange-yellow plates (m. p. 215—220°), which are insoluble in water and sparingly soluble in alcohol, ether, and benzene, but more easily in glacial acetic acid.

β-Mononitrophenanthrene, $C_{14}H_9(NO_2)$, differs but little in appearance and solubility from the α-compound, although it is somewhat less soluble in ether than the latter. It is obtained in smaller quantity than either of the other isomerides, and melts at 127°. Unlike the α-compound, it is only acted on with difficulty by alcoholic ammonium sulphide, and is best reduced by tin and hydrochloric acid in alcoholic solution. *β-Amidophenanthrene hydrochloride* forms a moderately stable crystalline mass, which is sparingly soluble in water. *β-Amidophenanthrene* crystallises from alcohol in small brilliant plates. *β-Mononitrophenanthrene* is more difficult of oxidation than the α-compound, and gives a product which crystallises from glacial acetic acid in brilliant orange-yellow needles (m. p. 260—266°).

γ-Mononitrophenanthrene, $C_{14}H_9(NO_2)$, crystallises in small brilliant plates (m. p. 170°), which are of a darker yellow, and are more sparingly soluble in ether and alcohol than the α- or β-compound.

γ-Amidophenanthrene hydrochloride, $C_{14}H_9(NH_2).HCl$, obtained by reduction of the nitro-compound with alcoholic ammonium sulphide, forms yellowish brilliant crystals. The free base resembles the α- and β-compounds.

On oxidation with chromic and glacial acetic acids, γ-nitrophenanthrene gives a compound which crystallises in dark orange-yellow needles (m. p. 263°), which are only very sparingly soluble in alcohol, but easily in glacial acetic acid.

By the direct nitration of phenanthrenequinone, Anschütz and Schultz (*Ber.*, **9**, 1404) have obtained a mononitrophenanthrenequinone (m. p. 257°), which appears to be isomeric and not identical with the

compounds described above, for its solubility in glacial acetic acid is very different from that of the compound derived from β-mononitrophenanthrene, which in other respects it most nearly resembles. From this it would appear that there are no less than four isomeric mononitrophenanthrenequinones. T. C.

Constitution of Anthrarufin and Oxyanthrarufin. By C. Liebermann and J. Dehnst (*Deut. Chem. Ges. Ber.*, **12**, 1287—1294). When sodium α- and β-anthracenesulphonate are boiled with crude nitric acid, the sodium salts of the corresponding anthraquinonesulphonic acids are formed. They are deposited on cooling, and may be purified by draining off the nitric acid, drying at 120°, and recrystallising from water. To distinguish these isomeric acids, the authors propose to term the acid from which chrysazin is derived χ-anthraquinonesulphonic acid, and to prefix the letter ρ to the acid corresponding to anthrarufin.

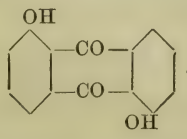
Sodium χ-anthraquinonedisulphonate, $C_{14}H_6O_2(SO_3Na)_2 + 4H_2O$, crystallises in yellow prisms, which are sparingly soluble in water. Sodium ρ-anthraquinonedisulphonate forms pale-yellow plates, containing $5H_2O$. It dissolves freely in water.

When these sodium salts are fused with potash, chrysazin and anthrarufin are formed in the first instance, but if the operation is carried on at a high temperature, the fused mass assumes a blue colour, and dissolves in water, yielding a blue solution. The blue coloration indicates the presence of oxychrysazin and oxyanthrarufin. In order to obtain satisfactory yields of these two substances, the mixture must be brought to the required temperature as rapidly as possible.

Oxychrysazin, $C_{14}H_8O_5$ (from the χ-sulphonic acid), is deposited from an alcoholic solution in small red needles, which sublime without decomposition. The triacetyl-derivative, $C_{14}H_5O_2(OAc)_3$, forms yellow needles.

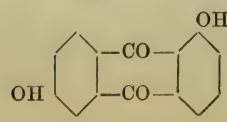
The trioxyanthraquinones derived from the χ- and ρ-sulphonic acids are identical. The solutions of the two substances exhibit the same absorption spectra, and yield similar precipitates with certain metallic salts, *e.g.*, with lead acetate a bluish-violet, with aluminium acetate a violet-red, and with baryta-water a blue precipitate. A solution of the trioxyanthraquinone in very dilute alkali has a red-violet colour, which changes to blue on the addition of more alkali.

χ- and ρ-anthraquinonesulphonic acids are decomposed by long continued fusion with potash, yielding salicylic and metahydroxybenzoic acids, no parahydroxybenzoic acid is formed. The preceding experiments have led the authors to adopt the following formula for anthrarufin :—

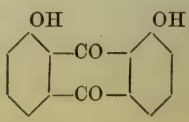


. The constitution of chrysazin is

either



or



When anthraquinonemonosulphonic acid is fused with potash at a high temperature, it splits up, yielding benzoic acid, protocatechuic acid, and a third acid which has not yet been identified.

W. C. W.

Chronology of the Isomeric Purpurins and the actual Relations of Anthrapurpurin, Isopurpurin, and Flavopurpurin. By H. Morton (*Chem. News*, **39**, 255).—The author explains that in 1870, Perkin referred to a new colouring matter which he found in purifying artificial alizarin. He studied this body, and in 1872 read a paper "On a Secondary Colouring Matter produced in the preparation of Alizarin from Anthracene," and gave its formula as $C_{14}H_8O_5$; and in 1873 he published a long article on the same substance, to which he gave the name of "*anthrapurpurin*."

Two months after Perkin's second publication, G. Auerbach announced the discovery of a new substance from artificial alizarin, which he called *isopurpurin*, and as he did not know of Perkin's prior publications, he assumed the substance described by Perkin as anthrapurpurin in his third publication to be the same as his *isopurpurin*, and claimed priority, and into this error he has led subsequent writers.

If Auerbach had prepared the same substance as that called anthrapurpurin by Perkin, it is evident he had no claim to priority, but as a matter of fact his isopurpurin was proved by Schunck and Roemer's researches published in 1875 to be composed principally of another new body called by them "*flavopurpurin*."

The author and his friend Geyer repeated the treatment of artificial alizarin both by Perkin's and by Auerbach's methods, and whilst they found anthrapurpurin to be a homogeneous substance as described by the former, they isolated two very different bodies from the isopurpurin described by the latter, one of which was anthrapurpurin and the other flavopurpurin, together with a trace of alizarin.

Rosenstiehl (*Bull. Soc. Chim.*, **29**, 408) further verifies the author's results. He says "I was not slow in discovering the presence of 15 per cent. of alizarin" in isopurpurin. W. T.

Compounds of the Terpenes with Hydrochloric Acid. By W. A. Tilden (*Chem. News.*, **39**, 256).—When dry hydrogen chloride is passed into cooled turpentine-oil (b. p. 156°), the well-known solid terpene mono-hydrochloride, $C_{10}H_{17}Cl$, melting at 125°, and boiling at about 210°, is produced, together with a liquid substance which is a mixture of the mono- and di-hydrochlorides, and found in company with cymene, which is always present in turpentine-oil. The author verifies the observation of Berthelot, that the mono- and di-hydrochlorides of terpene combine and become liquid, and doubts the existence of a liquid mono-hydrochloride.

If turpentine-oil be dissolved in benzene or carbon bisulphide, and dry hydrogen chloride passed through the mixture, the solid monohydrochloride is again produced; but if it be dissolved in a menstruum which contains either water or the elements of water, such as alcohol, ether, or acetic acid, the *di-hydrochloride*, $C_{10}H_{18}Cl_2$, is formed, and on standing is deposited as crystals which melt at 48°. The author found

it impossible to convert the mono- into di-hydrochloride by the action of hydrochloric acid on it. These two hydrochlorides are of entirely dissimilar constitution. By the action of soda, the mono-hydrochloride is decomposed, yielding a crystalline camphene, whilst the di-hydrochloride yields chiefly terpinol, $C_{10}H_{17}(OH)$.

The di-hydrochloride may also be prepared by the action of hydrogen chloride on crystallised terpin hydrate, on terpinol, and on the alcoholic or ethereal solution of the terpenes of higher boiling points than turpentine oil, whilst the mono-hydrochloride cannot be produced from these terpenes.

The di-hydrochlorides obtained from all the different terpenes possess the same properties, with the exception of that produced from "sylvestrene," the terpene which was discovered by Atterberg in Swedish turpentine, and recognised by the author in Russian turpentine. Its crystals melt at 72° to 73°. It is decomposed by alkali but yields a hydrate which is apparently not common terpinol; it is possible this substance may be capable of being converted into a new terpin.

By prolonged boiling with water, the di-hydrochloride is resolved into hydrochloric acid and terpinylene, $C_{10}H_{16}$, which boils at 176°, a portion of which is converted at the same time into viscid polymerides, but the terpinylene cannot again be made to combine with hydrochloric acid to form the crystalline di-hydrochloride. W. T.

Terebenthene Di-hydrochloride. By J. de Montgolfier (*Compt. rend.*, **89**, 102—103).—By the action of sodium on terebenthene di-hydrochloride a mixture of the hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{20}$, is obtained. The product after treatment with hydrochloric acid yields a liquid boiling at 170° (corr.), having the properties of Berthelot's "hydride of terpilene" obtained by the action of hydriodic acid on terebenthene. It is a mobile liquid of heavy camphorous odour; its sp. gr. is 0·8179 at 0° and 0·8060 at 17·5°. The results of analysis correspond with the formula $C_{10}H_{20}$. L. T. O'S.

Isomerides of Borneol. By J. de Montgolfier (*Compt. rend.*, **89**, 101—102).—By the hydrogenation of dextrorotary camphor two isomerides of borneol are obtained, one dextrorotary, the other lævorotary. The latter when oxidised is converted into the original dextrorotary camphor; it is very unstable, and readily attacked by nitric or chromic acid. In order to ascertain whether a lævorotary camphor yields a lævo- and a dextrorotary borneol, experiments were made with *camphol de garance*, and the results correspond with those obtained from a dextrorotary camphor; from the analogy between the results, the existence of two isomeric borneols would appear probable. L. T. O'S.

Formulæ of Quercetrin and Quercetin. By C. Liebermann and S. Hamburger (*Deut. Chem. Ges. Ber.*, **12**, 1178—1187).—Numerous formulæ have been assigned to these two bodies by various chemists, among which we have the following:—For quercetrin, $C_{16}H_{18}O_{10}$ (Bolley); $C_{36}H_{40}O_{21}$ and $C_{36}H_{38}O_{21}$ (Rigaud); $C_{35}H_{36}O_{20} + xaq$, $C_{29}H_{30}O_{17}$ and $C_{33}H_{30}O_{17}$ (Hlasiwetz); $C_{18}H_{20}O_{10}$ (Stein); $C_{19}H_{18}O_{10}$ (Zwenger and and Dronke); $C_{15}H_{16}O_9$ (Löwe). For quercetin, $C_{24}H_{20}O_{11}$ and $C_{24}H_{18}O_{11}$

(Rigaud); $C_{26}H_{20}O_{12}$ (Wurtz); $C_{26}H_{16}O_{10}$ (Gerhardt); $C_{23}H_{16}O_{10}$ and $C_{27}H_{18}O_{12}$ (Hlasiwetz); $C_{20}H_{14}O_9$ (Stein); $C_{26}H_{20}O_{12}$ (Zwenger and Dronke); $C_{15}H_{12}O_7$ (Löwe); $C_{27}H_{20}O_{12}$ (Latour and Magnier). The authors endeavour to settle the formulæ of these compounds, not only by direct analysis, but also by an examination of a number of their derivatives. For this purpose they have limited their investigation to the quercitrin and quercetin obtained from quercitron. The method employed for the preparation and purification of the quercitrin was that of Zwenger and Dronke, viz., the bark was boiled for six hours with alcohol (85 per cent.), after which half the alcohol was distilled off and the residues filtered; some glacial acetic acid was then added, and the impurities precipitated by an alcoholic solution of lead acetate, excess of the latter being avoided; the precipitate was washed with very dilute acetic acid and the filtrate treated with sulphuretted hydrogen to remove lead, and afterwards evaporated to dryness. The residue was exhausted with alcohol, and the quercitrin reprecipitated with water and crystallised from boiling water.

Quercitrin, $C_{36}H_{33}O_{20}$, thus obtained crystallises in pale-yellow, silvery needles or plates. The formulæ adopted for this and the following compound are derived from the analysis of the substance after drying at 125—130°.

Quercetin, $C_{24}H_{16}O_{11}$, was obtained from quercitrin by boiling its aqueous solutions with very dilute sulphuric acid. It separates from the liquid as a lemon-yellow crystalline powder, which is very sparingly soluble in water.

The above formulæ for quercitrin and quercetin were confirmed by a quantitative determination of the following reaction :—$C_{36}H_{38}O_{20} + 3H_2O = 2C_6H_{14}O_6 + C_{24}H_{16}O_{11}$, according to which 100 parts of quercitrin should yield 60·76 parts of quercetin and 46·08 parts of isodulcite. Experiment gave 61·21 and 46·37 respectively. The authors cannot confirm Rigaud's statement, that a hydrate of grape-sugar and not isodulcite is obtained by this reaction, nor the assumption of Hlasiwetz, that different sugars are contained in different quercitron barks, nor Löwe's results, according to which quercitrin is not a glucoside, but a hydrate of quercetin.

Acetylquercetin, $C_{24}H_{14}(C_2H_3O)_2O_{11}$, is easily obtained by boiling quercetin with acetic anhydride and sodium acetate. It crystallises from alcohol in white needles (m. p. 197°). The number of hydroxyl-groups was also determined by Schiff's magnesia method.

Dibromoquercetin, $C_{24}H_{14}Br_2O_{11}$, was prepared by adding 2 parts of bromine, drop by drop, to 3 parts of quercetin mixed with glacial acetic acid. It crystallises in bright yellow needles.

Dibromacetylquercetin, $C_{24}H_{12}Br_2(C_2H_3O)_2O_{11}$, white needles (m. p. 218°).

Sodium-quercetin, $C_{24}H_{14}Na_2O_{11}$, was previously obtained by Hlasiwetz. The composition of these substances shows that quercetin contains two hydroxyl-groups.

Tetrabromquercetrin, $C_{36}H_{34}Br_4O_{20}$, was obtained by adding an excess of bromine to quercitrin, care being taken to keep the liquid cool. It forms a bright yellow crystalline mass, and is rather soluble in alcohol; it dissolves in alkali with a brownish-yellow colour. That this com-

pound was a substituted derivative of the glucoside was proved by the fact that, on warming with dilute sulphuric acid for three hours, it gave isodulcite and *tetrabromoquercetin*, $C_{24}H_{12}Br_4O_{11}$, the latter of which crystallises in yellow needles.

Tetrabromodiacetyl-quercetin, $C_{24}H_{10}Br_4(C_2H_3O)_2O_{11}$, crystallises in white needles (m. p. 227°).

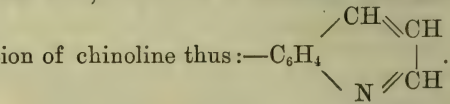
Potassium quercitrin, $C_{36}H_{36}K_2O_{20}$, was obtained as a yellow precipitate by adding a cold solution of alcoholic potash to a cold saturated alcoholic solution of quercitrin. Treated with acids in the cold, it yields quercitrin. Quercitrin, therefore, contains the same number of acid hydroxyl-hydrogen atoms displaceable by potassium as quercetin. This, however, appears inexplicable, if we assume that in glucosides the saccharyl-radicle is attached, as in ethereal salts, to the acid radicle by means of the hydroxyl-oxygen atoms of the latter. But it has been previously shown (*Annalen*, **196**, 336) in the case of xanthorhamnin, that the hydroxyls of the saccharyl-radicle probably take part in the formation of glucosides. This is confirmed by the fact that numerous metallic derivatives of the sugars are known, and experiment has shown that isodulcite forms such metallic compounds with sodium and lead.

Sodium-isodulcite, $C_6H_{12}Na_2O_6$, was obtained as a white crystalline precipitate by adding an alcoholic solution of sodium ethylate to a cold saturated solution of isodulcite in absolute alcohol.

From the foregoing results the following formulæ are assigned to quercitrin and quercetin respectively:—$C_{24}H_{14}O_9 : (O.C_6H_{12}O_4)_2 : O$, and $C_{24}H_{14}O_9(OH)_2$.

Quercetin and rhamnetin, $C_{12}H_{10}O_5$ or $C_{24}H_{18}O_{10}$, are evidently nearly related to one another. The much greater solubility of xanthorhamnetin in respect to quercitrin is due to its containing 4 mols. of isodulcite, whereas quercitrin contains but 2 mols. T. C.

Synthesis of Chinoline. By A. Baeyer (*Deut. Chem. Ges. Ber.*, **12**, 1320—1323).—*Dichlorochinoline*, $C_9H_5NCl_2$, is formed by the action of phosphorus pentachloride to which a few drops of phosphorus oxychloride have been added, on hydrocarbostyril. This substance melts at 104°: it is soluble in alcohol, ether, and benzene, and forms a sparingly soluble crystalline salt with hydriodic acid. When dichlorochinoline is treated with glacial acetic acid which has been saturated with hydriodic acid, chinoline is formed. The author represents the constitution of chinoline thus:—



W. C. W.

Oxidation of Quinine. By S. Hoogewerff and W. A. van Dorp (*Deut. Chem. Ges. Ber.*, **12**, 1287).—The authors point out two errors in their previous communication on this subject (*Ber.*, **12**, 158), viz., the ratio between the potassium permanganate and quinine sulphate used in the experiments was 8·5—9·5 to 1, and not 8·5 to 16 as previously stated. The statement that a mixture of pyridinecarbonic acids is formed by the oxidation is incorrect, only pyridinetricarbonic acid being obtained. W. C. W.

Formation of Cinchomeronic Acid from Quinine, and its Identity with Pyridinedicarbonic Acid. By H. Weidel and M. v. Schmidt (*Deut. Chem. Ges. Ber.*, **12**, 1146—1153).—It has been previously shown that cinchonine and cinchonidine both yield the same products on oxidation with fuming nitric acid, viz.:—Cinchoninic acid, $C_{10}H_7NO_2$; chinolic acid, $C_9H_6N_2O_6$; cinchomeronic acid, $C_7H_5NO_4$ (not $C_{11}H_8N_2O_6$, as stated in a previous communication, *Annalen*, **173**, 96); and oxycinchomeronic acid, $C_8H_5NO_6$. Quinine, on the other hand, yields only cinchomeronic acid, when treated in a similar manner. It forms white prismatic needles, which melt at 250°, with partial decomposition, and dissolve but very sparingly in boiling water. It is a dibasic acid, and forms two classes of salts.

Sodium-hydrogen cinchomeronate, $C_7H_4NaNO_4$, forms almost colourless prismatic needles, which soon become opaque on exposure to the air: they are easily soluble in water, but only sparingly in alcohol.

Sodium cinchomerate, $C_7H_3Na_2NO_4$, forms small, brilliant needles, which are easily soluble in water and in alcohol, and contain 2 molecules of water of crystallisation, which they lose at 110°. *Calcium cinchomerate* is $C_7H_3CaNO_4 + 3H_2O$.

Cinchomeronic acid, when subjected to dry distillation with caustic alkali, gives pyridine: it is therefore a pyridinedicarbonic acid, $C_5H_3N(COOH)_2$ (see also Skraup, *Ber.*, **12**, 243), but is isomeric, and not identical with the pyridinedicarbonic acid obtained by Dewar from picoline, as the latter acid melts at 241°, and gives with ferrous sulphate a characteristic red coloration. Nor is it identical with the acid $C_7H_5NO_4$, prepared by Ramsay and Dobbie (*Ber.*, **11**, 324), by the oxidation of quinine with potassium permanganate, which also gives a red coloration with ferrous salts; nor with the pyridinetricarbonic acid obtained by Hoogewerff and van Dorp (*Ber.*, **12**, 185) from the same alkaloïd, for this acid melts at 244°, and is easily soluble in water and in alcohol.

When an aqueous solution of sodium cinchomeronate is reduced by sodium-amalgam, cinchonic acid, $C_7H_6O_5 + \frac{1}{2}H_2O$, is obtained. This reaction is analogous to that which occurs in the case of picolinic acid (Weidel, *Ak. Ber.*, 1879), thus:—

$$\underset{\text{Picolinic acid.}}{C_6H_5NO_2} + H_2O + H_4 = NH_3 + C_6H_8O_3;$$

$$\underset{\text{Cinchomeronic acid.}}{C_7H_5NO_4} + H_2O + H_2 = NH_3 + \underset{\text{Cinchonic acid.}}{C_7H_6O_5}$$

On dry distillation, cinchonic acid splits up into carbonic anhydride and *pyrocinchonic acid*, $C_6H_6O_3$ (and not $C_{10}H_{10}O_5$, as previously stated), which crystallises in rhombic pearly plates (m. p., 90°; b. p., 214°, uncorr.), and has a sweet taste and an acid reaction. Vapour-density = 4·16, calculated for $C_6H_6O_3$ = 4·35.

Chinolic acid, heated with concentrated nitric acid in closed tube at 170°, gives cinchomeronic acid, which explains the fact observed by Koenigs (*Ber.*, **12**, 97), that cinchoninic acid, on oxidation with nitric acid, yields cinchomeronic acid as well as chinolic acid.

T. C.

Composition of Cinchonine. By Z. H. Skraup (*Liebig's Annalen*, **197**, 352—374).—The results of a number of careful analyses show that the formula of *pure* cinchonine is $C_{19}H_{22}N_2O$. The *platinum double salt*, $C_{19}H_{22}N_2O(HCl)_2PtCl_4$ forms thin plates of a yellow colour, and is anhydrous. The *neutral sulphate* $(C_{19}H_{22}N_2O)_2H_2SO_4 + 2H_2O$, melts at 196° (uncorr.), and is very hygroscopic. The *neutral hydrochloride* and *hydriodide* were also prepared, and found to bear out the formula given above. The former contains 2 mols. H_2O, the latter only $1H_2O$.

Commercial cinchonine contains another body, $C_{19}H_{24}N_2O$, which has been called hydrocinchonine, but which the author proposes to term *cinchotine*. It crystallises in very small prisms, which are anhydrous, and melt at 277·3° (corr.). Its *sulphate* and a *platinum double salt* have been prepared. G. T. A.

Oxidation-products of Cinchonine. By Z. H. Skraup (*Liebig's Annalen*, **197**, 374—384).—The author has investigated the action of potassium permanganate on cinchonine, the proportions employed being 144 of the former to 100 of the latter, and special precautions were taken to prevent any rise of temperature. The products obtained were cinchotenine, $C_{18}H_{20}N_2O_3$, identical in properties with that of Caventou and Willm (*Annalen*, *Sup.* **7**, 247), and formic acid. Weidel's cinchonic acid (*Annalen*, **173**, 76), therefore, must be formed by the further decomposition of cinchotenine, and hence its formula cannot be $C_{20}H_{14}N_2O_4$, but must be halved. The alkaloïd found by him amongst the products of decomposition, also, must from its origin be placed between cinchotenine and the acids formed. G. T. A.

Cinchonidine. By Z. H. Skraup and G. Vortmann (*Liebig's Annalen*, **197**, 226—243).—The authors have prepared the pure base from the commercial sulphate; it crystallises from alcohol in short prisms, sparingly soluble in ether. Its sulphuric acid solution exhibits no fluorescence. It melts at 210·5°, solidifying at 197—198° to form a white mass. Analysis of the base shows its composition to be $C_{19}H_{22}N_2O$, and not $C_{20}H_{24}N_2O$ (Hesse, *Annalen*, **135**, 339).

The *platinum salt*, $C_{19}H_{22}N_2O(HCl)_2PtCl_4 + H_2O$ is obtained as a yellow precipitate, by adding platinic chloride to a solution of the base in hydrochloric acid. It crystallises from hot water in golden-yellow prisms, resembling the cinchonine salt. The *hydrochloride* $C_{19}H_{22}N_2OHCl.H_2O$ is obtained in compact, well-formed crystals, or in tufts of slender prisms.

The *neutral sulphate* $(C_{19}H_{22}N_2O)_2H_2SO_4$, forms slender needles, uniting to form a gelatinous mass. The physical properties of this substance are such as have been ascribed by Hesse (*Ber.*, **10**, 2156, and **11**, 1164) to homocinchonidine sulphate, and, like the latter, loses its water of crystallisation on exposure to dry air, and takes up water from moist air. Commercial cinchonidine sulphate crystallises with 6 mols. of water, and after drying takes up 2 mols. of water from the air, a behaviour due to the presence of quinine sulphate. These observations, together with the results of analyses of cinchoni-

dine, tend to show that homocinchonidine is pure cinchonidine, as supposed by Skraup (*Ber.*, **11**, 311).

On oxidation with potassium permanganate, cinchonidine yields formic acid, and a base isomeric with cinchotenine, called *cinchotenidine* by the author. Absolute alcohol dissolves it sparingly, and it crystallises from the solution in long, thread-like needles; from solution in hot water it separates in long compact monoclinic prisms, which are seldom united, and are transparent whilst in the mother-liquor, but become white when removed. As crystallised from water, its composition is $C_{18}H_{20}N_2O_3 + 3H_2O$. Its aqueous and sulphuric acid solutions exhibit fluorescence, which may be due to the presence of impurities, as commercial cinchonidine sulphate was used, and further, the fluorescence decreases with each crystallisation. The aqueous solution has a neutral reaction; it is but sparingly soluble in cold water, the best solvent being dilute alcohol. It is also dissolved by dilute acids and by alkalis, being precipitated from its solutions in the latter by carbonic anhydride. With silver, copper, and lead salts, it reacts in a manner analogous to cinchotenine. It melts at 256° (corr.), decomposing at the same time with evolution of gas. Its action on polarised light is exactly the opposite of that of cinchotenine.

The *sulphate* is obtained in a crystalline state with great difficulty; it forms small white prisms, having the composition

$$(C_{18}H_{20}N_2O_3)_2H_2SO_4 + 2\tfrac{1}{2}H_2O.$$

The *platinum salt* $(C_{18}H_{20}N_2O_3)_2(HCl)_4.PtCl_4$, forms large orange-red leaflets, and sometimes more compact crystals, belonging to the rhombic system.

This oxidation of cinchonidine takes place in a manner analogous to that of cinchonine, and may be formulated thus: $C_{19}H_{22}N_2O + HO = C_{18}H_{20}N_2O_3 + CH_2O_2$. P. P. B.

Chemistry of the Bile. By G. Hüfner (*J. pr. Chem.* [2], **19**, 302—309).—Statistics are given of the successful and unsuccessful attempts made to prepare glycocholic acid from ox-bile by the direct addition of ether and hydrochloric acid (*J. pr. Chem.* [2], **10**, 267). The success of the process seems to depend on the nature of the food of the animal, the bile of which is examined. (In a note by Kolbe, facts are detailed which seem to show that a deficient supply of common salt with the food diminishes the bile acids, and that in such cases Hüfner's method for preparing glycocholic acid is unsuccessful.)

It is shown that after adding ether and hydrochloric acid to ox-bile, and thus precipitating glycocholic acid, the presence of taurocholic acid and of choline may be readily proved in the upper layer of ethereal liquid.

Cholic acid was prepared from glycocholic acid by boiling the latter with dilute baryta-water, filtering hot, adding hydrochloric acid after cooling, and recrystallising the precipitated acid from hot alcohol. *Ethyl cholate* was prepared by a modification of Tappeiner's method (this Journal [2], **12**, 256). When heated in a sealed tube with concentrated alcoholic ammonia for six days at 130°, it is converted into *cholamide*, $C_{24}H_{41}NO_4$, which may be obtained as brilliant needle-

shaped crystals (m. p. about 130°) on adding water to the product, boiling, and filtering. Cholamide is very hygroscopic; it dissolves easily in alcohol, less easily in ether, and only to a small extent in boiling water, from which solution it separates on cooling.

M. M. P. M.

Preparation of Crystalline Albumin-compounds. By E. Drechsel (*J. pr. Chem.* [2], **19**, 331—335).—The author finds that the crystals from Para nuts described by Schmiedeberg, and said by him to be obtained with difficulty, can be easily prepared by precipitating a solution of the crystalloïd with carbonic anhydride, digesting with magnesia and water, filtering, and placing the liquid in a dialyser, which is then floated on absolute alcohol. The water quickly passes through the dialyser and crystals separate out from the solution. Urea was obtained from blood by this method of "alcoholic dialysis," and the author proposes to apply it to the preparation of crystalline compounds of albumin. M. M. P. M.

Regeneration of Albumin from Peptone. By F. Hofmeister (*Bied. Centr.*, 1879, 25).—By the action of acetic anhydride on fibrin-peptone, Henninger has obtained an albuminous substance, somewhat analogous to syntonin (this Journal, Abstr. 1878, 802). A similar product is obtained when purified fibrin-peptone is heated for one hour at 140°, or for a shorter time at 160—170°. The peptone becomes brown, evolves alkaline fumes, and is partly converted into a substance which is analogous to albumin. The heated mass is to a great extent soluble in cold water; the insoluble portion consists of a flocculent substance, which gives the reactions of freshly precipitated protein. A. J. C.

Protagon. By A. Gamgee and E. Blankenhorn (*Deut. Chem Ges. Ber.*, **12**, 1229—1234).—Diacanow, Hoppe-Seyler, and Thudicum have thrown doubt upon the existence of protagon, which Liebreich (*Annalen*, **134**, 24—44) discovered in the brain substance, and to which the formula $C_{116}H_{241}N_4O_{22}P$ was attributed. In consequence of this, protagon has since been regarded as a mixture of lecithin and cerebrin, a position which the physical properties of these bodies make untenable. Further, the authors have prepared large quantities of protagon from the brain of oxen, horses, and dogs, by a modified form of Liebreich's method: the analyses lead to the adoption of the formula $C_{160}H_{308}N_5PO_{35}$ for this body. Its physical properties are those attributed to it by Liebreich, *i.e.*, it is a white, non-hygroscopic substance, which may be obtained in the crystalline state by suspending it in alcohol, and heating it for some time at 45°. When heated to 150° it becomes brown, and at 200° it begins to melt, forming a brown syrup. By long-continued boiling with ether, it is decomposed.

P. P. B.

Physiological Chemistry.

Feeding Experiments with Sheep. By E. Sonntag, von Shönberg, and H. Lorenz (*Bied. Centr.*, 1879, 25—27).—Three concurrent series of experiments made, with the object of ascertaining the effect of various kinds of fodder in increasing the quantity of the wool and the weight of the sheep, but the results obtained seem to have been very undecided. A. J. C.

Influence of the Surrounding Temperature on the Tissue Change of Warm-blooded Animals. By C. Voit and C. Theodor (*Bied. Centr.*, 1879, 20—24).—The results of these experiments are in accord with those obtained by Pflüger (this Journal, 1876, 106) and by Colasanti (*idem*, 1877, 327), that the absorption of oxygen and excretion of carbonic anhydride increases as the temperature is artificially lowered. The increase in the amount of carbonic anhydride excreted was especially noticeable in an experiment which Voit made on a man who had been kept in a fasting condition and in complete repose for six hours:—

Temperature	4·4°	6·5°	9·0°	14·3°	
CO_2 in grams	210·70	206·00	192·00	155·1	
Nitrogen in urine	4·23	4·05	4·20	3·81	
Temperature	16·2°	23·7°	24·2°	26·7	30·0°
CO_2 in grams	158·3	164·8	166·5	160·00	170·6
Nitrogen in urine	4·00	4·40	3·34	3·97	—

As Voit has already shown that oxygen is not generally the primary cause of the decomposition of albumin, fatty bodies, and carbohydrates in the animal body, it follows that an increase in the supply of oxygen, arising from a more rapid respiration, as is the case in a cold atmosphere, cannot be the cause of the increased metamorphosis at the low temperature.

The variation in the rhythm of breathing, which is quicker at a low temperature, has not such an influence (as Lossen has shown) on the amount of carbonic anhydride exhaled as the change in temperature. Voit proves that the specific heat of the body does not tend to increase the excretion of carbonic anhydride, for in the above experiment the temperature of the body had not altered. Moreover, experiments on sleeping guinea pigs showed, on the contrary, that with a low animal heat, as is the case in these animals, there was a diminution in the amount of carbonic anhydride exhaled. It was remarked, however, that the absorption of oxygen did not diminish, for whereas in the waking state the proportion of oxygen absorbed to that contained in the excreted carbonic anhydride was as 100 : 80, it had now become as low as 100 : 44.

Voit is inclined to describe the increase in weight of animals during sleep to the absorption of oxygen, and in the case of guinea pigs it is due to the accumulation of a considerable quantity of glycogen.

The amount of oxygen absorbed varies according as the reaction

occurs between it and a carbohydrate, albumin, or fat. In the case of a carbohydrate, 100 p. c. of the oxygen absorbed would be found in the carbonic anhydride excreted, whilst albumin would give 83 p. c., and a fatty body, 73 p. c. As from each of these substances many intermediate products can be formed, according to the temperature and state of repose of the body, so Voit considers that the oxygen consumption and carbonic anhydride excretion can be regarded only in a very small degree as a measure of the intensity of the tissue metamorphosis.

He agrees with Pflüger and Schuler, that the muscles are essentially the centre of the carbonic anhydride formation, and consequently of the heat production. In proof of this he cites the case of a man who, having entirely lost the power of will and feeling, excreted during 12 hours 250 grams only of carbonic anhydride, whilst a sound man in the same period excreted 403 grams.

At low temperatures, the above experiments on the man show that the non-nitrogenous substances are decomposed in the greater quantity, whilst there is a constancy in the decomposition of albuminous substances, that is, in the amount of urea excreted. A. J. C.

Source of Hippuric Acid in the Urine of Herbivorous Animals. By O. Loew (*J. pr. Chem.* [2], **19**, 309—312).—The author has proved the presence of quinic acid in hay (the process of preparation therefrom is detailed), and thinks it probable that the hippuric acid which is present in the urine of the herbivora, is one of the products of the decomposition of this body. M. M. P. M.

Formation of Urea in the Animal Organism. By O. Schmiedeberg and Walter (*Bied. Centr.* 1879, 70).—Urea is probably formed in the organism from ammonium salts, and—contrary to the views of Salkowski (*idem*, 1878, 513)—under normal conditions the nitrogen of the albuminoïds is converted into ammonia, and thence into urea.

Phenylamine is not decomposed in the organism; but benzylamine is split up in the same way as methylamine, &c. A. J. C.

Analysis of Silk Cocoons. By A. Renouard (*Bied. Centr.*, 1879, 72).

	In the entire cocoon.	In the inner layer.	In the outer layer.
Gummy substance....	29·30	31·47	27·72
Fibroïn	70·70	68·33	73·28

The gummy substance was obtained by boiling the cocoon with a strong solution of soap, then washing with boiling acetic acid; the insoluble residue was calculated as fibroïn. Mulder's analysis of silk is said to be incorrect; he stated that silk contained 19—21 per cent. glutinous substance, and 24—25 per cent. albumin. A. J. C.

Chemistry of Vegetable Physiology and Agriculture.

Relation of Oxygen to the Life of the Microzoa. By Nencki (*J. pr. Chem.* [2], **19**, 337—358).—It is stated by Gunning (*ibid.*, **19**, 266), as the results of a long series of experiments, that, in the case of putrescible liquids contained in sealed glass vessels, putrefaction either never sets in or if it does is speedily suspended: this appears to be directly contrary to a statement (*ibid.*, **19**) of the author based on the experiments of Jeanneret, viz., that living organisms can, in the absence of oxygen, both induce and bring to completion the decomposition of relatively large quantities of organic matters. The author briefly criticises this objection, showing (1) that the exclusion of air by hermetically closing the vessel introduces the condition of the prevention of the escape of volatile products, which by consequent accumulation may end or prejudice the life of Bacteria, &c.; and (2) that the liquids used to induce putrefaction did not contain those special ferment organisms whose life is independent of a supply of oxygen. He then proceeds to describe the methods by which he subjected the point in question to a further investigation.

(*a.*) Quantities of 25 c.c. of a putrescible fluid, together with a small piece of pancreas, or a few drops of pancreas-extract, were introduced into glass bulbs of 50 c.c. capacity, blown on to the end of tubes of 1 cm. diameter; these were exhausted of air and sealed. Eight of these were kept submerged in water at 40° C., for intervals varying from a few days to three weeks. In all cases putrefaction set in, the contents of the bulbs becoming turbid, smelling strongly and exhibiting pressure on opening. The greater part of the proteïd matter was decomposed, with formation of peptones, amido-acids, indole and volatile fatty acids (as ammonium salts) in relatively larger quantity.

(*b.*) The putrescible fluid was contained in a bulb blown on to the end of a tube, a narrow neck intervening between the bulb and the upper part of the tube. Into this neck fitted the lower end of a glass rod, ground so as to effect perfect closure; the upper end passing through the cork by which the tube is closed. By special manipulation the bulb and its contents were entirely deprived of oxygen, the stopper was inserted, and an alkaline solution of pyrogallol was then introduced so as to fill the tube to some distance above the neck. Under these conditions of oxygen-exclusion (and at 40° C.), putrefaction was invariably observed to set in within 24 hours, and after a further lapse of a day, peptones, ammonia, and volatile fatty acids were present in quantity.

(*c.*) In these experiments the further condition was introduced of the freedom of escape of the volatile products of putrefaction. The apparatus by which this was effected consisted of a flask of about one liter capacity, continuous at its neck with a bend at right angles to its length, and this with a bulbed **U**-tube, terminating in a long narrow tube, bent twice at right angles; the whole being constructed in one piece. The putrescible fluid (500 c.c.) was introduced into the flask, and the whole apparatus and its contents were deprived of oxygen;

an atmosphere of nitrogen being then substituted; the lower portion of the **U**-tube was filled with pyrogallol solution, the extremity of the delivery tube submerged in mercury, and finally, the flask surrounded with water at 40°. The following is a brief history of an experiment: Started 16th November with 500 c.c. pancreas extract (5 c.c. containing 0·1058 gram proteïd matter). On the following day considerable evolution of gas which smelt strongly and contained much hydrogen. This ceased on the 24th; on the 26th the flask was emptied of its contents and these analysed. They were free from albumin, but contained peptones, leucine, indole, and a large quantity of volatile fatty acids. The organisms taking part in these decompositions are figured and described.

The author considers that these results justify his original statement. On the other hand he corroborates the observation of Gunning that the putrefaction of liquids contained in sealed vessels takes place only up to a certain point, the attainment of this limit being evidenced by the liquid becoming clear, the organisms losing their activity and sinking to the bottom. The explanation of this lies in the poisonous action on an organism, of its own excreta, which is probably true for the lower as for the higher forms of life.

In reference to the probable cause of the non-occurrence of fermentation in several of Gunning's experiments, viz., the absence of "anaërobic" organisms, the microscopic examination of fluids, putrefying under exposure to the air, demonstrated the following points: the skin which forms on the surface contains Microbacteria and Bacillariæ only, whereas in the deeper parts of the fluid, protected by this skin from access of oxygen, different forms of Coccus are found, together with the knobbed form of Bacteria, these latter being essentially anaërobic organisms. The same definite localisation of the "organised ferments" is observed in liquids putrefying under the influence of pancreas-extract, whether at the ordinary temperature or at 40°. In the latter case, in which the process is more rapid, the localisation is most sharply defined from the second to the fourth day. Further light is thrown on the conditions of life of these anaërobic organisms by an experiment of Kaufmann's. To a boiling solution (10 per cent.) of 230 grams gelatin, 10 c.c. of pancreas-extract were added, and the whole was cooled to 40°, at which temperature it was maintained, in an apparatus similar to that described by Jeanneret (*ibid.* [2], **15**, 353). Putrefaction set in on the third day; and on the seventeenth day 33 c.c. of gas had been evolved; on the twelfth the evolution underwent a sudden increase. The gas was now collected daily and analysed so far as regards the percentage absorption by potash: the unabsorbed portion consisted of nearly pure hydrogen.* To select a mean result:—The evolution ceased on the twenty-first day, and the liquid contained ammonia, acetic acid, and glycocine, in addition to peptones. From the above it appears that not only are the anaërobic organisms in question capable of inducing and completing the putrefactive decomposition of large quantities of organic matter, but they do so after having been exposed to the boiling temperature.

* The occurrence of hydrogen as a product of this decomposition stands in opposition to the observation of Jeanneret.

It may be therefore stated, generally, that proteïds are brought into putrefaction by anaërobic organisms, and are through their agency resolved into products, such as glycocine, indole, phenol, acetic and butyric acid (together with a certain quantity of carbonic acid and ammonia) and that of these, the fatty and amido-acids, are susceptible of complete oxidation to carbonic anhydride and water (and ammonia), under the influence of other forms of microzoa whose life depends on a supply of oxygen. The relation of the functions of these two groups of microzoa is in close analogy with that of Torula to Mucor and Mucedo in the fermentation of sugar.

The digestive process which occurs in the large intestine is a putrefactive decomposition which must be referred to anaërobic organisms, and one which occurs under the favourable condition of the absorption of the products by the mucosa. There are also certain pathological conditions of the body which are attended by putrefaction in absence of atmospheric oxygen. The author gives full details of the chemical and microscopic examination of pus taken from two subjects, shortly after death in the one case from acute cystitis, in the other from pleuritis. From both he succeeded in isolating phenol and indole; and he also observed the identity of the organisms present with the anaërobic microzoa previously described. The pus corpuscles had for the most part undergone no change of form, whence it must be concluded that the putrefaction, which had been going on for months, was extremely tardy in character; this is probably in consequence of the prevention of the escape of the products.

In conclusion, the author states that he is satisfied that these microzoa are present in normal tissues and glands. C. F. C.

Preliminary Notes on the Absorption of Selenium by Plants. By A. Cameron (*Chem. News*, **39**, 243).—Experiments have been made by investigators on the Continent with the view of replacing some of the elements natural to plants by others of a similar nature, and thus to introduce Mn_2O_3 in place of Fe_2O_3, and sodium in place of potassium, but always with negative results.

In 1863, the author showed that potassium was capable of being replaced by rubidium. The analogy between sulphur and selenium suggested the possibility of the latter wholly or partially replacing the former in plants. As all the sulphur found in plants either in the albumin or the mineral salts, enters the plants as sulphates, such as those of lime or potash, the author made his experiments by watering during four weeks one half of a sod 3 ft. × 1 ft. and 2 ft. in depth, in which some leguminous plants had just made their appearance, with a weak solution of K_2SeO_4 and the other half with water, 20 grams of K_2SeO_4 in all being employed. The author, after washing the plants thoroughly with water, detected the presence of selenium in them.

This experiment showed (1) that the plants absorbed and retained the selenium, although the author did not determine in what state it existed there, and (2), that the selenium seemed neither to injure nor to improve the growth of the plants. W. T.

Analyses of Cattle Fodder. (*Bied. Centr.*, 1879, 32—34).—Microscopic examination, by Wien, of No. 1 Thorley's, showed it to consist of equal parts of bruised maize and carob seeds: an ethereal oil of a plant of the *Umbelliferæ* had been added to it. No. 2 Gibbs' also contained a large proportion of carob seeds.

	No. 1.			No. 2.
	Wein.	Nessler.	Mayer.	Mayer.
Water	13·72	—	12·9	12·6
Albuminoïds	11·75	13·2	9·4	11·5
Fat	4·28	4·24	3·6	6·4
Non-nitrogenous extractive matter	67·24	—	66·9	49·5
Fibre	—	—	3·6	12·6
Ash	3·01	—	3·6	7·4

Both of the above were of English manufacture.

Henrich has also examined a "rape-seed" cake, which consisted for most part of uncrushed seeds of 16 varieties of field-weeds, which are comparatively worthless as a cattle feed. A. J. C.

Seed of Sorghum Vulgare. By F. Storer and D. S. Lewis (*Bied. Centr.*, 1879, 73).

	In the ripe seed.		In unripe seed, 1876.		
	1875–6.	1876.	In blossom.	After blossoming.	Partly ripe.
Proteïn	7·84	8·63	7·38	9·65	9·72
Non-nitrogenous extractive matter and fat	82·37	81·01	59·93	58·40	69·18
Cellulose	7·51	7·46	28·26	25·42	16·32
Ash	2·28	2·90	4·43	6·53	4·78

A. J. C.

Analysis of Shave Grass. By F. Storer and D. S. Lewis (*Bied. Centr.*, 1879, 73).—The fresh shoots contain about 86 per cent. water.

	Seed-bearing shoots.	Barren shoots.
Equisetum Arvense—		
Proteïn	14·62	23·26
Cellulose	14·72	17·31
Fat	2·68	5·31
Non-nitrogenous extractive matter	55·43	42·00
Ash	12·55	*12·12
Equisetum Silvaticum—		
Proteïn	13·58	22·91

A. J. C.

* Contains 30·21 per cent. silicic acid.

Composition of Candle-nuts. By L. Mutschler and C. Krauch (*Bied. Centr.*, 1879, 71).

	Proteïn.	Fat.	Ash.	Fibre.	Non-nitrogenous extractive matter.	Water.
The peeled nut ..	22·75	60·93	3·42	2·67	6·54	3·69
Expressed cake ..	47·31	14·74	7·07	3·71	18·00	9·71

The oil contains C = 76·82, H = 11·91, O = 11·27; and consists of 85·95 per cent. oleic acid, 16·52 per cent. of other fatty acid, and 3·01 per cent. glycerol. It has a low solidifying point, and can be used as a lubricator and for soap-making, but not for varnishes, &c.

The amount of proteïn in the expressed cake is nearly equal to that in earth nut and cotton-seed cakes, and although no substance of a deleterious nature could be detected in the nut, yet as some of the *Euphorbiaceæ*—to which family it belongs—contain poisonous substances and oils having a purging action, it is doubtful whether candle-nut cake can be used as a cattle fodder. A. J. C.

Analysis of Hops. By L. Siewert (*Bied. Centr.*, 1879, 54—55). —*West Prussian.*—The following analyses are representative of the eleven samples examined:—

Moisture	11·80	13·90	12·00	10·00	9·90	10·73
Sand	1·46	1·90	2·56	1·90	2·90	1·60
Ash	5·72	8·40	6·10	6·20	6·60	5·80
Organic matter	81·02	75·80	79·34	81·90	80·60	81·87
Fibre	16·60	15·58	15·20	15·62	15·20	18·20
Albuminoïds	14·88	13·39	12·94	16·01	13·39	15·75
Tannin	1·43	0·83	1·01	1·50	1·34	0·90
Soluble in ether	17·46	13·43	18·84	19·03	18·39	11·30
Soluble in alcohol	17·20	12·33	13·20	14·50	11·10	10·19
Total extract	34·66	25·76	32·04	33·53	29·49	21·49

The oil and resinous matter are more completely extracted by using ether first and then alcohol: but the amount extracted by ether alone is a good criterion of the quality of hops, and in good samples it appears to be about 20 per cent.

E. Weiss (*idem*, 8, 75) suggests the use of alcohol of 90 per cent. for extraction, and in the seven varieties examined, the amount of extract obtained from the entire cone varied from 26·33—33·23 per cent.

A. J. C.

Cohesive Power of Soils. By F. Haberlandt (*Bied. Centr.*, 1879, 6—9).—The author's method for ascertaining the cohesive power of a soil consists in determining the breaking weight of a cylindrical mould of the damp soil. Applying this method to several kinds

of soils, the results show that a soil which contains much humus, lime, and clay has the greatest, whilst a micaceous sandy soil has the least cohesive power. The addition of caustic lime to a soil appears to be especially active in decreasing its cohesive power, which is also influenced by the mechanical structure of the soil, and not by the degree of fineness alone.

The cohesive power of a soil steadily decreases as the amount of water is increased; but every soil, even the most binding kind, has a point of lowest cohesive power. A. J. C.

Heat-capacity of Soils. By C. Lang (*Bied. Centr.*, 1879, 9—12).—The author suggests to ascertain the heat-capacity of a soil by calculation from the specific heat of its several constituents, instead of directly determining it in the soil itself. For example, the specific heat of a soil directly determined was ·267, and ·262 by calculation, as under:—

	Soil contained grams.	Specific heat of each constituent.	Specific heat of each constituent in the soil calculated from the quantity present.
Water	0·027	1·0000	0·0270
Silicic acid	0·398	0·1885	0·0752
Calcium carbonate	0·427	0·2064	0·0879
Magnesium carbonate	0·073	0·2599	0·0190
Alumina	0·052	0·2170 (calc.)	0·0113
Ferric oxide	0·053	0·1634	0·0086
Humus	0·172	0·5000	0·0860
Total	1·202		0·3150

$$\text{Heat-capacity} \ldots = \frac{0{\cdot}3150}{1{\cdot}202} = 0{\cdot}262.$$

The following specific heats are also given:—

	Quartz sand.		
	Coarse.	Fine.	Pulverised (not quite pure).
Mean results	0·198	0·194	0·209

The degree of fineness therefore had no influence on the heat capacity of the sand.

The specific heat of the various constituents of soils differs very little if referred to the volume; *i.e.*, the product of the specific gravity into the specific heat is tolerably constant. A. J. C.

Experiments with Artificial Manures. By G. v. Massenbach (*Bied. Centr.*, 1879, 16—18).—The author has not been very successful in his experiments with artificial manures. He is of opinion that the addition of a small quantity of artificial manure has very little effect in increasing the crop; that with strong nitrogenous manures, such as Chili saltpetre, the manner in which the soil is prepared is of more importance than an increase in the quantity of the manure. In

experiments with various kinds of wheat, the increase in the crop was in no instance sufficient to defray the extra outlay for artificial manure.

For winter sowing, it is recommended to add to the soil per "morgen" 75 kilos. of ammonio-phosphate containing 7 per cent. N, and 10 per cent. phosphoric acid: for summer sowing, 50 kilos. of Chili saltpetre; superphosphate is said to be quite worthless for this purpose, but can be used on poor sandy soils for the potato crop and winter sowing. A. J. C.

Manure Experiments with Bone-meal Superphosphates. By E. Wein (*Bied. Centr.*, 1879, 12—14).—A paper confirming by analytical results the usually accepted opinion, that the wheat crop is improved in quantity and quality by manuring the soil, especially soils that are poor in humus, with nitrogenous superphosphates.

With Various Kinds of Potash Salts. By E. Ebermann (*ibid.*, 14—15).—*Oats* (sown down with clover grass) after sugar beets on heavy red clay soil.

Plot.	Kilos.	Produce in grain kilos.
1.....	13·5 of potash as crude sulphate	600
2.....	13·0 „ kainite.....	575
3.....	13·0—15 „ carbonate (wood ashes)	650
4.....	unmanured	550

Sugar beets after unmanured wheat on humus clover soil. Each plot also received 150 kilos. "Ammonio-Superphosphate" (analysis not given).

Plot.	Kilos.	Produce. Kilos.	Gravity (Brix).	Sugar, p. c.	Non-saccharine matter.	Sugar factor.
1	13·5 of potash as crude sulphate.....	6,750	15·6°	12·66	3·06	81·75
2	13·0 of potash as kainite ..	6,100	16·1	13·17	2·93	81·80
3	13·0—15 of potash as carbonate (wood-ashes)	6,375	15·9	12·63	3·33	79·40
4	Unmanured	5,935	14·7	11·34	3·36	77·70

A. J. C.

Effect of Artificially Manured Barley on the Composition of the Wort. By C. Lintner, Krandauer, and Trieber (*Bied. Centr.*, 1879, 18—20).—Four fields of about one-third hectare each were sown with barley with the addition of artificial manures, and the results obtained are shown in the following table:—

	1. Potassium sulphate.	2. Superphosphate.	3. Peruvian guano.	4. Unmanured.
In 100 parts by weight of air-dried barley.				
Water	18·508	16·891	17·063	16·570
Dry substance	81·492	83·109	82·937	83·430
In 100 parts by weight of dried barley.				
Ash	3·259	2·953	3·373	2·938
Nitrogen	1·730	1·615	1·775	1·558
Proteïn compounds	10·816	10·095	11·095	9·731
Phosphoric acid	0·807	0·859	1·28	0·780
In 100 parts of air-dried malt.				
Water	11·035	5·047	7·473	—
Dry substance	88·965	94·053	92·527	—
Extract	58·786	66·666	63·070	—
The wort from 100 parts of dried malt contained.				
Extract	66·077	70·882	68·164	—
Sugar	32·264	29·052	27·019	—
Dextrin	22·326	22·298	27·455	—
Ash	1·140	1·276	1·129	—
Proteïn compounds	2·908	2·964	3·058	—
Nitrogen	0·466	0·474	0·489	—
To 1 part of sugar there was non-saccharine substance	1·050	1·440	1·500	—
In 100 parts dried malt.				
Proteïn substances	9·000	7·540	9·386	—
Nitrogen	1·540	1·306	1·501	—

Hence there are three artificial manures that are capable of increasing the amount of nitrogen in barley, and giving a crop containing an average of 10·5 per cent. of proteïn substances, an amount required for malt-barley. A. J. C.

Cultivation and Preservation of Maize. By J. Moser (*Bied. Centr.*, 1879, 44—50).—This paper gives the results of an extensive series of experiments on the cultivation of various kinds of the seed and on the preservation of the produce. A. J. C.

Preservation of Beet-leaves and the Preparation of Brown-hay from Maize. By W. Gerland and J. Roberts (*Bied. Centr.*, 1879, 27—32).—As a winter fodder for cattle, the authors recommend the well-known plan of preserving beet-leaves in pits, which are covered with earth about a foot deep.

The authors give in detail the results of their experiments, which show that a mixed diet containing a large proportion of beet-leaves

which had been preserved in the manner described, is the best kind of fattening fodder for sheep and cattle.

A similar process which is also applicable to other kinds of plant-fodder is described for the preparation of brown-hay from maize-leaves. A. J. C.

Analyses of Some Species of the Gourd Family. By F. H. Storer and D. S. Lewis (*Bied. Centr.*, 1879, 41—42).—The author has examined four species of the gourd family, including the ordinary yellow field pumpkin (*Cucurbita maxima*), the marrow pumpkin (*Cucurbita Pepo medullosa*), and his analyses show that in many respects they resemble turnips in composition. The rind contains more proteïn-substances than the fruit. They form a good fattening fodder for cattle, but the seeds, although readily eaten, appear to be prejudicial to the secretion of the milk. A. J. C.

Composition of the Ashes of Wheat-bran, burned under a Steam-boiler. By S. F. Peckham (*Chem. News*, **39**, 244).—This material was pure white and vesicular, resembling "Cooper River phosphate." It appeared to have been completely fused, and was free from charcoal and sand. The analysis was made by Miss Cora J. Brown.

Its sp. gr. was 2·34, and hardness 3·5 to 4. It was composed of: Cl, 0·612 per cent.; SO_3, 0·151; SiO_2, 0·627; P_2O_5, 48·328; K_2O, 6·659; Na_2O, 6·664; CaO, 10·615; MgO, 18·980; Fe_2O_3, 2·015; H_2O, 0·438; sand, 3·170 = 98·259. The author considers that the analysis indicates the following composition:—KCl, 1·2887; K_4SiO_4, 2·5936; K_3PO_4, 5·8337; Na_3PO_4, 11·7370; H_3PO_4, 9·3721; $CaSO_4$, 1·9567; $Ca_3(PO_4)_2$, 18·2342; $Mg_3(PO_4)_2$, 41·4600; $Fe_2(PO_4)_2$, 3·8058; H_2O, 0·4379; sand (insoluble residue), 3·1700 = 99·8897.

The substance contained no CO_2, and the smallness of the proportion of chlorine was due no doubt to the chlorides having been volatilised by the high temperature to which the ash was subjected. The presence of free phosphoric acid may be questioned. W. T.

Analytical Chemistry.

Estimation of Nitrogen. By J. Ruffle (*Chem. News*, **40**, 17).—In the *Chemical News*, **25**, 189, the author mentioned that by modifying the soda-lime process for nitrogen determinations, as much as 80 per cent. of the nitrogen of a nitrate could be determined, whether present in conjunction with ammoniacal salts or otherwise, and that under certain circumstances as much as 94 per cent. of nitrate had been converted into ammonia in such combustion process. In the present paper he publishes a number of nitrogen estimations of various substances. The results, which appear very satisfactory, give the nitrogen when present as a simple nitrate, or as a lower oxide of nitrogen, also when the nitrate is mixed in a complex substance like an artificial manure, or gunpowder, and whether with or without the presence of organic matter. The process is said to

ensure the ready and complete estimation of the total nitrogen in a compound or mixture in whatever form the nitrogen may be present, *i.e.*, as an albuminoïd compound, ammoniacal salt, or as an oxide of nitrogen.

The author intends shortly to make the method known. D. B.

Determination of Nitrogen in the Analysis of Agricultural Products. By S. W. Johnson and E. H. Jenkins (*Chem. News*, **40**, 28—30).—The authors replace the mixture of caustic soda and lime known as soda-lime, and used in chemical analysis for nitrogen determinations, by a mixture of equal volumes of dry sodium carbonate and slaked lime. This soda-lime is to be recommended, because the materials for making it, sodium carbonate and quick-lime, are everywhere procurable in a state of purity; the preparation of many pounds of the mixture may be accomplished in an hour or two with little trouble; and the resulting soda-lime is extremely convenient to use, not absorbing moisture in the mixing, and never swelling in the tube so as to obstruct it on application of heat.

It is well known to chemists that a number of experimenters have failed to obtain with the soda-lime method as high results on meat, milk, and similar substances, as by the use of the so-called absolute method, in which the organic body is burned with copper oxide, and its nitrogen measured directly in the state of gas. The authors therefore have endeavoured to investigate the correctness of these two modes of analysis, to study the sources of error to which they are severally subject, and to learn what is essential to bring out the greatest accuracy of which they are susceptible. They have been led to the conclusion that with the substances above named, both methods when properly worked give nearly accordant results. Dried blood, dried white of egg, and maize-fibrin, containing 12 or more per cent. of nitrogen, have yielded from one to two-tenths of a per cent. less of nitrogen by the soda-lime combustion than by the absolute method. Moreover, it is observed that this discrepancy is no more due to any fault of the soda-lime process than to the errors of the absolute method,—errors caused probably by the impossibility of removing the last traces of common air from the mixture, either by long-continued transmission of pure carbonic acid or by exhaustion with the mercury pump, or by both conjointly. A large number of analyses illustrate a fact, which is general in the authors' experience, viz., that the agreement of several determinations made upon one substance is usually closer by the soda-lime than by the absolute method.

This fact goes far to show that the soda-lime process is, to say the least, equal in accuracy to the absolute determination.

As to the working out of the soda-lime method, the following results have been arrived at:—(1.) Contrary to what is commonly stated, fine pulverisation of the substance to be analysed is not necessary. If the substance will pass through holes 1 mm. in diameter, it is fine enough. (2.) Neither the highest heat possible to obtain in an Erlenmeyer gas combustion-furnace, nor a long layer of strongly heated soda-lime, nor these two conditions united, occasion any appreciable dissociation of the ammonia formed in the combustion. (3.) The

use of pure sugar or of oxalic acid as a diluent does not in any way affect the result. (4.) Iron tubes of proper length may be substituted for glass, but more time is required for the combustion. (5.) A suitable length of the anterior layer of soda-lime must be secured in order to get a good result. (6.) The long anterior layer must be brought to a full red heat before heating the mixture, and must be so kept throughout the combustion. (7.) No fumes or tarry matters, indicative of incomplete combustion, should appear in the bulb-tube or receiver. (8.) Equally good results are obtained whether the mixture is made intimately in a mortar, or more roughly by stirring with a spatula in a capsule or scoop, or by mixing in the tube with a wire. (9.) The ammonia is received in a bulb-tube or flask containing standard hydrochloric acid, and the excess of the latter measured by a standard solution of ammonia, using tincture of cochineal as the indicator.

In conclusion, the authors mention that the purity and uniformly satisfactory qualities of the new soda-lime have greatly facilitated the work of the present paper. D. B.

Use of Sulphuretted Hydrogen in the Dry Way in Analysis. By A. Carnot (*Compt. rend.*, 89, 167—170).—The author draws attention to Ebelmen's proposal (*Ann. Chim. Phys.*, 1849) to use sulphuretted hydrogen in the dry way in mineral analysis. He finds that by heating many substances in a current of the dry gas, they are readily and completely converted into sulphides, even if they resist the action of the strongest acids. This method may be employed for the quantitative determination of many metals, since most of the sulphides thus obtained have a definite composition, or may be brought into this condition by ignition in a current of hydrogen. Cobalt and tin do not give definite sulphides when treated in this way.

C. H. B.

Water Analysis. By E. Bohlig (*Zeits. Anal. Chem.*, 1879, 195—198).—The author in a previous paper has put forward reasons (*Zeits.*, 1878, 301) to prove that the analytical results obtained from a water after it has been boiled, cannot be considered as applicable to the water in its original state, since ebullition brings about certain decompositions and changes. At a temperature slightly above 100° C., calcium carbonate and magnesium sulphate are converted by double decomposition into magnesium carbonate and calcium sulphate, owing to the greater affinity of calcium for the sulphate radicle. Therefore, in a solution containing equivalent quantities of sulphuric acid, lime, and magnesia, and excess of carbonic acid, the salts present will be calcium sulphate and magnesium carbonate. If, however, the free carbonic acid is removed at any temperature below 100°, calcium carbonate is precipitated, since it is the most insoluble compound which can be formed, and magnesium sulphate remains in solution. The author purifies water on this principle by adding magnesium hydrate, which at ordinary temperatures forms with the free carbonic acid magnesium carbonate, and this decomposes the calcium salts. If the carbonic anhydride is removed by simple boiling, the lime and carbonic acid are in most cases entirely precipitated as calcium carbonate if mag-

nesia is present in sufficient quantity; but when the boiling is continued, especially when the quantity of soluble salts present is considerable, the boiling point becomes higher, and calcium sulphate is formed, partly owing to the magnesium carbonate losing carbonic anhydride and being changed into the more insoluble basic carbonate, and partly owing to the affinity of calcium for the sulphate radicle. This is proved by boiling magnesium sulphate solution with calcium carbonate, and passing the steam into lime-water; it is found that carbonic anhydride escapes and calcium sulphate remains in solution, whilst basic magnesium carbonate, or if the boiling point has risen considerably, even magnesium hydrate itself remains in the precipitate. This explains why bitter waters, like the Hunyadi János, deposit basic magnesium carbonate when boiled; the carbonic acid may all be free or combined with magnesia, and the double decomposition between calcium sulphate and magnesium carbonate will be hindered by the increased solubility of calcium carbonate due to the quantity of sodium chloride and sulphate present. For this latter reason, the separation of calcium carbonate on addition of magnesium hydrate to such a water is incomplete.

The basic magnesium carbonate separated by continued boiling is too sparingly soluble to decompose calcium sulphate in the water on cooling: but the carbonate formed by passing carbonic anhydride into boiling water in which magnesium hydrate is suspended, decomposes calcium salts very easily, 1 part, reckoned as magnesia, is soluble in 20,000 of water. It is evident then that it is useless to attempt to decide by boiling a water whether the magnesium salt it contains is carbonate or not, since any water containing calcium sulphate refuses to yield a magnesium carbonate precipitate when it is boiled. It also results from the above facts that if the magnesium found corresponds with the acid-neutralising power of the water, the magnesium is present entirely as carbonate, and only an excess of magnesium beyond this limit can be combined with stronger acid radicles.

Hence in the results of analysis, magnesium sulphate, nitrate, and chloride must not be entered with calcium carbonate. The decomposition occurring between calcium carbonate and magnesium sulphate in a water containing excess of carbonic acid is proved by adding lime-water to such a water, first before and then after the addition of the magnesium sulphate: in the first case calcium carbonate is precipitated, in the second case, owing to the conversion of calcium carbonate into calcium sulphate, no such precipitate is formed.

F. C.

Detection and Estimation of Nitrous Acid in Potable Waters, Acids, &c. By A. R. Leeds (*Chem. News*, **40**, 38, and 61—63).—I. *With Metadiamidobenzene.*—This method depends upon the observation originally made by Griess, that diamidobenzoic acid is an extremely delicate test for nitrous acid, giving in very dilute solutions of this body an intense yellow colour. Later, Griess proposed to employ instead of this compound another allied substance, metadiamidobenzene, which is more readily prepared, and is twice as sensitive as diamidobenzoic acid. The latter indicates the presence of one-fifth mgram. N_2O_3 in a litre of water; the former of one-tenth or one part in

10 millions. Preusse and Tiemann have given the details essential to the employment of this compound in quantitative colorimetric determinations (*Ber.*, **11**, 627), but instead of using cylinders of colourless glass as recommended by these authors, comparison-tubes and the colourless comparator (*Proc. Amer. Chem. Soc.*, **2**, 1) may be more conveniently employed. Inasmuch as the tints of colour developed by the metadiamidobenzene are so analogous to those exhibited by a dilute caramel solution, that they can be closely copied by the latter, the author uses such a caramel solution in the glass wedge of the colour comparator for estimations of nitrous acid. The same wedge provided with a different scale, answers for the determination of minute amounts of ammonia by the Nessler reagent.

Amount of Nitrous Acid in Potable Waters.—The author found in the water of the Passaic, as drawn from the hydrant in the laboratory, 0·12 per cent. N_2O_3 in one million. Griess has emphatically insisted upon the importance of determining the nitrous acid in potable waters, and upon their unfitness for household use when they contain nitrous acid; and it is thought that in cases like the above, the nitrous acid should always be separately looked for and removed if found. It is an error to accept or condemn a drinking water from the determinations of ammonia and albuminoïd ammonia alone. These results should be checked by independent determinations of the nitric and nitrous acids. By the aid of improved methods, this can be as readily done as the corresponding estimations of ammonia and albuminoïd ammonia, and a skilful water analyst should be able to perform all four within the space of two hours.

II. *With Potassium Iodide.*—The well-known method of Trommsdorf is of colorimetric character. The potable water to be examined is treated with a solution of zinc iodide, starch, and sulphuric acid, which develops a blue colour if nitrous acid is present. The amount of nitrous acid corresponding to this colour is found by striking in distilled water containing these reagents the same tint with a standard nitrous acid solution. It is essential that the unknown and known solutions should be prepared at the same time, and that they be equally exposed to the action of the air, and acted on by light of equal intensity and for an equal length of time. The object of the author's investigations in this direction is to point out the importance and necessity of these precautions.

As a preliminary determination, the limits of sensitiveness of the zinc-iodide starch solution were investigated, and the rapidity with which it would undergo change in presence of acid in diffused daylight. It is shown that the reaction ceases when waters contain 0·05 mgram. N_2O_3 in 100 c.c. With regard to the effect of colouring matters and organic impurities on the rate of change of acid solutions of the soluble iodides, a number of experiments were made, from which the following conclusions are drawn:—(1.) When the solutions to be titrated are colourless and contain no compounds, organic or inorganic, which would affect the percentage of dissolved oxygen, the determination may be made by the colorimetric method. (2.) When the solutions are coloured or contain organic or other bodies capable of absorbing oxygen, the air must be entirely removed from the liquids

in order to obtain good results, and an absolute volumetric determination is essential. As to the degree of concentration at which soluble iodides will cease to remain unchanged in presence of free acid, even when out of contact with air, it is mentioned, that in the absence of air and presence of carbonic acid, decomposition of an acid solution of potassium iodide occurs when the concentration has attained to some point between one-third and one-tenth the weight of the water employed. During the investigation of this point, a compound of starch was formed, which, from its deportment with reagents, and more especially from its turning blue on absorption of oxygen, may probably be regarded as a hydriodide of starch. An attempt would have been made to study it further, had it not been for the difficulty of satisfactorily isolating a body, which changed so readily on exposure to air into ordinary starch iodide. D. B.

Determination of Phosphoric Acid. By S. W. Johnson and E. H. Jenkins (*Chem. News*, **40**, 39—40).—The authors have devised a method for estimating phosphoric acid, which is said to require less than half the time and labour necessary for the molybdic acid method, to be scarcely less accurate and generally applicable. Stolba has shown that pure ammonio-magnesium phosphate can be determined by titration as well as by weighing, one molecule of pure salt requiring two molecules of hydrochloric acid to destroy its alkaline reaction. The authors have taken advantage of this circumstance. The standard acid used in other volumetric work answers perfectly for this purpose. A strong, nearly saturated, solution of ammonium tartrate, free from carbonic acid, and a solution of a magnesium salt are also necessary. The latter is prepared by dissolving 10 grams of magnesium sulphate and 195 grams ammonium chloride in 1 litre of water, 10 c.c. of this solution contain twice the amount of magnesium necessary to precipitate 0·1 gram phosphoric acid. A suitable amount of phosphate (in most cases 1 gram is a convenient quantity) is dissolved in hydrochloric acid, the solution nearly neutralised with ammonia, and ammonium tartrate solution is added, 10 c.c. at a time, until the solution remains perfectly clear when slightly alkaline. A suitable quantity of the magnesium mixture is then added, and the liquid either vigorously stirred with a rod, or, if the precipitation is made in an assay-flask, shaken occasionally. When the precipitation is nearly complete, enough ammonia must be added to make the liquid strongly alkaline, and it must be left at rest for six to twelve hours, then filtered and the precipitate washed with equal parts of strong alcohol (85—90 p.c.) and water. No pains need be taken to detach the precipitate from the glass. When the dish and precipitate are washed until the washings no longer react alkaline, the filter and precipitate are returned to the beaker or flask, a little water and a few drops of cochineal tincture are added, and the whole is titrated. This is best done by adding an excess of standard acid at once, stirring so that all the precipitate shall be wetted with it, and after it has stood for a few minutes, titrating back with standard alkali.

Some investigations of the authors, which are not yet completely worked out, lead them to hope that ammonium tartrate may be suc-

cessfully substituted for ammonium citrate for bringing precipitated or reverted phosphates into solution. This step would still further simplify the analyses of superphosphates, since the entire phosphoric acid, soluble, reverted and insoluble, could be quickly estimated in a single portion. Since ammonio-magnesium phosphate is largely soluble in ferric and aluminic solutions, containing insufficient ammonium tartrate, it is necessary, in presence of iron, to add ammonium tartrate more than enough to produce a reddish-yellow solution, enough, in fact, to make a greenish-yellow solution. D. B.

Estimation of the Value of Superphosphates. By H. Albert and L. Siegfried (*Zeits. Anal. Chem.*, 1879, 220—224).—Further experience leads the authors to prefer ammonium citrate to ammonium tartrate solution in the analysis of superphosphates. The citrate shows a decidedly greater solvent and decomposing power than the tartrate, when acting under similar conditions on neutral and hydrated phosphates: the reason probably being that calcium tartrate is precipitated and surrounds the particles of phosphate, whereas the soluble calcium citrate exerts no such hindering effect. Superphosphate freshly prepared from phosphorite, gave almost identical results with the solutions of the ammonium salts, but the differences were greater when richer phosphates and higher temperatures were employed. The authors summarise in a table the results of a number of comparative analyses, in which the solutions of the two salts are allowed to act for one hour at temperatures of 17—20°, and of 95—100° respectively. The solutions were prepared so that a litre contained 400 grams of citric acid and 240 grams of tartaric acid respectively, first saturated with ammonia, and then supersaturated by the addition of 10 c.c. more of ammonium hydrate solution. Of these solutions 40 c.c. were gradually poured upon 1 gram of superphosphate, which was then finely powdered in a mortar, and raised without dilution into a flask: after an hour's digestion, the whole was made up to 100 c.c., filtered, and 50 c.c. of the filtrate was precipitated with magnesia mixture; the precipitate was filtered off after four hours, washed with dilute ammonia, and dissolved together with any residue in the beaker in nitric acid: after saturating this solution with ammonia and acidifying, the phosphate present was titrated with uranium solution. The analysis was usually finished in about seven hours, but when traces of phosphate only were present, the precipitation was allowed to continue for a night. The addition of 10 c.c. of ammonia was found sufficient to keep the solution of a superphosphate containing 20 per cent. of soluble phosphoric acid alkaline when heated for an hour to 95°. The citrate showed in all cases a superior solvent power, and at the higher temperature it dissolved even the difficultly soluble phosphate in phosphorites to which sufficient sulphuric acid had been added to combine with 90 per cent. of the calcium present. Basic and neutral phosphates freed from water of hydration partially at 120° C. or entirely by ignition, were found to be correspondingly insoluble. The solvent power of the tartrate at 95° was only equal to that of the citrate at 17—20°. The latter temperature is that best suited for extracting the phosphate of manurial value. Commercial

bone-ash and bone-black, and precipitated phosphates dried at 100°, contain very little phosphoric acid which is soluble in the citrate solution: but all freshly precipitated and undried phosphates showed a solubility which indicated that they were mobile, assimilable compounds. Hence the preparation of hydrated phosphates for manures may be undertaken in competition with natural phosphates. In making superphosphate from mineral phosphates, coprolites, and bone-black, over two-thirds of the total calcium present must be combined with sulphuric acid to render almost all the phosphoric acid present soluble in the citrate solution. It is possible that superphosphate, soluble in water, is best suited as manure for certain soils, but it is beyond doubt that the manurial value usually depends upon the quantity of hydrated phosphate present, as measured by the citrate solution, and in that case the argillaceous phosphates found at home may compete at about half the cost with the purer imported phosphates. Wagner has shown that the phosphate soluble in water is rapidly precipitated when coming in contact with the soil, and therefore cannot present great advantage over the hydrated phosphates. It appears that the superphosphate is more active when applied in coarse powder than when very finely ground. The authors consider that the estimation of the phosphate soluble in water, does not give the full manurial value of a superphosphate, unless it is supplemented by the citrate treatment as described above. F. C.

Estimation of Phosphoric Acid in Fish Guano. By E. Dietzell and M. G. Kressner (*Zeits. Anal. Chem.*, 1879, 225—230).—Fish guano has been prepared from sprats and herrings, from the refuse of sardines, and from shrimps. The materials used largely for its preparation are also the unsaleable fish taken in the cod fishery, and the whale when deprived of its whalebone and oil, and the seal after losing its oil and skin. The valuable constituents of the fish guano appear to be its calcium phosphate and its nitrogen. Schumann directs the phosphoric acid to be estimated as in bone-ash: the author has critically examined the methods hitherto used. In samples of "Polar" and "Lofoden" guano, the author found that the phosphate was not all present as calcium phosphate, but some of it as alkaline phosphate: the aqueous extracts were neutral, and contained about 0·8 per cent. of phosphoric acid, and from 1·24—1·63 per cent. of potash, but usually no calcium, iron, or magnesium. When the fish guano was incinerated and ignited and then dissolved in dilute nitric acid, a considerable quantity of the alkaline phosphate escaped estimation, probably by being converted into other modifications of phosphate: this loss was diminished by incinerating at as low a temperature as possible; it was prevented by evaporating the ash twice with strong nitric acid before precipitating the phosphoric acid, or by dissolving the guano in hydrochloric acid without previous incineration, and either titrating the phosphoric acid directly with uranium solution, or precipitating with magnesia mixture after separating the iron and calcium. This source of error has been previously noticed by Fresenius and by Gilbert, who avoided it by oxidising the organic portions of the guano by fusion with sodium carbonate and potassium chlorate or nitrate.

The authors tried this method, and found that its results closely agreed with those yielded by Liebig's process of oxidation by fusion with potassium hydrate, mixed with one-eighth its weight of potassium nitrate. These processes of oxidation yielded results which agreed well with those mentioned above in the case of "Polar" guano, but with "Lofoden" and "Peruvian" guano higher numbers were obtained, doubtless owing to the presence of organic phosphorus-compounds. These compounds could not be extracted by alcohol, ether, or ether-alcohol. The phosphorus in organic combination can scarcely have the same manurial value as the phosphates, and since it withstands oxidation by nitric acid, it cannot form soluble phosphate: hence the authors do not recommend the estimation of the phosphates in fish guano to be preceded by fusion with sodium carbonate and nitre, which would in some samples over-estimate its manurial value; nor can the estimation be preceded by simple incineration and ignition, which would usually yield too low results. The most trustworthy methods consist either in dissolving the guano directly in hydrochloric acid, or in evaporating the acid left on ignition twice with strong nitric acid before proceeding to the estimation. F. C.

A New Quantitative Analytical Method of Manifold Application. By A. Classen (*Zeits. Anal. Chem.*, 1879, 373—399).—In a former paper (*ibid.*, **182**), a method was described by the author for the estimation of manganese in the presence of ferric oxide and alumina, and in the present paper further applications of this method are given.

Estimation of Magnesium, and its separation from the Alkalis.—Soluble magnesium salts give with excess of potassium or ammonium oxalate soluble double salts, which are decomposed by the addition of strong acetic acid with separation of magnesium oxalate. The ammonium salt is generally to be preferred, since the magnesium precipitate then requires less washing, and also because the alkalis can be determined in the filtrate. About 25 c.c. of the aqueous magnesium solution are mixed with a solution of ammonium oxalate saturated whilst hot, the solution being added until the liquid becomes clear by formation of the double salt, and then as much more of the oxalate solution is to be added; or the solid ammonium salt may be dissolved by heating it in the magnesium solution. The liquid is then heated to boiling, an equal volume of 80 per cent. acetic acid added, and the boiling is continued with constant stirring for several minutes. A precipitate of heavy crystalline magnesium oxalate forms at once unless the quantity of magnesium present is very small, when the precipitate does not appear until after standing: in any case the vessel is covered with a watch-glass and allowed to stand for about six hours, at a temperature of 50°; it is then filtered off and well washed with a mixture in equal volumes of strong acetic acid, alcohol, and water. The oxalate is converted by the ignition in a platinum crucible into magnesium oxide, the precipitate being folded in the damp filter and gently heated in the covered crucible until vapours cease to appear. The lid is then removed, and the residue heated in the air until it is perfectly white: the crucible is then once more covered, and by strong ignition

the magnesium is entirely converted into oxide, which is weighed. The magnesium oxalate precipitate yields a dense heavy oxide, which is easily obtained as above without loss. By the precipitation of pure magnesium chloride in this manner and weighing the oxide produced, almost uniformly low results were obtained, the deficiency amounting to between 1—0·1 per cent. calculated on the oxide when about 0·05 to 0·2 gram of the oxide were present: in the presence of ammonium chloride, the deficiency was rather greater.

If the method is applied to the separation of magnesium from the alkalis, the alkalis may be present as chlorides, sulphates, or nitrates; but the magnesium oxalate must be precipitated from somewhat dilute solutions, otherwise the potassium salt and magnesium potassium oxalate will accompany the magnesium oxalate, and not being removed by the washing, will leave potassium carbonate with the magnesium oxide: to avoid this the liquid to be precipitated must be diluted to 50 c.c. and mixed with solution of ammonium oxalate (1 : 24) saturated in the cold, the magnesium oxide will then either be free from potassium or contain only imponderable traces detectable by the spectroscope. A loss is always incurred in precipitating the magnesium from dilute solutions, but this may be almost entirely avoided by adding to the cooled liquid from which the oxalate has been precipitated about one-third its volume of alcohol: this does not increase the quantity of potassium in the precipitate.

Separation of Ferric oxide and Alumina from Manganese, Zinc, Cobalt, and Nickel.—The ordinary method of precipitating the former oxides as basic acetates or basic salts, and determining the latter oxides in the filtrates, even when many times repeated, was imperfect, and was found in the case of nickel to incur a loss of 3·6 and 5·2 per cent. when one precipitation only had been made.

The separation of manganese by the new method has been fully described in the previous paper (*loc. cit.*). It can only be completely precipitated when sufficient zinc salt is present, and in the mixture of manganese and zinc oxides obtained the manganese may be titrated, or a known quantity of pure zinc salt may be added and the manganese calculated from the excess of weight of the precipitate above that of the zinc oxide present. In cases where the addition of zinc salt is injurious, magnesium chloride may be substituted, and the results are accurate, provided at least 1 mol. of magnesium oxide is present for every molecule of manganese oxide: calcium salts also serve a similar purpose. The results obtained were also accurate in a solution containing manganese, iron, aluminium, magnesium, and calcium phosphate.

The separation of zinc from iron and aluminium has been already pretty fully described (*loc. cit.*): the salts may be present as chlorides, bromides, nitrates, or sulphates; sulphates, however, require precipitation in more dilute solution because the potassium sulphate formed is rather difficultly soluble in acetic acid. All free acid must first be expelled by evaporating to dryness on the water-bath, and free sulphuric acid must be removed by heating more strongly on the sand-bath: the residue is then heated again for a short time in the water-bath, after the addition of a little dilute nitric acid or of about 10 c.c. of

bromine-water, this oxidation is necessary to prevent precipitation of ferrous oxalate with the zinc oxalate. A solution (1 : 3) containing about seven times as much neutral potassium oxalate as there are oxides present is added, and the whole is heated for a quarter of an hour on the water-bath, the undissolved ferric oxide being brought into solution by gradually dropping in acetic acid. When sufficient oxalate has been added, the liquid has a green colour, and is quite clear. The acetic acid is then added in quantity at least equal to the volume of the liquid, and the process carried out as was described for the precipitation of magnesium. The results of numerous test-analyses are tabulated, from which it appears that the error may be one either of excess or deficiency, and it usually varied from 0·5—1 per cent. on the quantity of zinc oxide present.

The separation of cobalt from iron and aluminium is effected in a precisely similar way to that of zinc : the last traces of sulphuric acid must be most carefully removed. The cobalt oxalate precipitate was first ignited, then well washed with boiling water, and the cobalt weighed as metal, after reduction by heating in a current of hydrogen. The results obtained were usually more satisfactory than those given for zinc, and varied to about the same extent.

In the separation of nickel, the nickel oxalate is precipitated in a crystalline condition only when the quantity of nickel precipitated is not very large, hence care must be taken not to use too large quantities of the substance. The results equalled those of cobalt in accuracy.

Estimation and separation of Copper.—If copper is the only metal present, it may be completely precipitated by adding to the strong neutral solution sufficient potassium oxalate, and after the liquid has stood until crystals of copper potassium oxalate have separated, adding a volume of acetic acid equal to that of the liquid. The precipitate is washed with the liquid already described, and the oxalates are decomposed by gentle ignition. The copper is then estimated either by dissolving the ignited residue in dilute sulphuric acid, and precipitating the metal on a platinum spiral by the galvanic current ; or the ignited residue is well washed, then ignited strongly in the air, and the resulting copper oxide is weighed.

When iron or aluminium is present, the copper may be precipitated as crystalline oxalate in precisely the same way as cobalt, nickel, and zinc. In this case the author ignited the oxalate gently in a platinum crucible, since the glaze of a porcelain crucible easily takes up copper, and the copper was then determined electrolytically : by this means pure copper is obtained, and zinc or magnesium may be determined in the liquid from which the copper has been precipitated. The results generally showed a deficiency of about 0·1—1 per cent.

When arsenic or antimony is present, as in fahlores, the precipitation is hindered and antimony is separated electrolytically with the copper. In cases where copper is to be estimated in the presence of arsenic, iron, and small quantities of antimony, the substance must be dissolved in nitric acid, evaporated to dryness, the residue mixed with excess of potassium oxalate, filtered hot, and the residue washed with water containing some potassium oxalate. The filtrate and washings

are then evaporated to 50 c.c., when the double copper salt crystallises and separates completely on the addition of one or two volumes of acetic acid. If much antimony is present, the finely-powdered substance is mixed with about four times as much ammonium chloride and gently heated in a covered crucible: almost the whole of the arsenic and antimony and the greatest portion of the iron are thus volatilised as chlorides, and the copper is then readily estimated as directed above.

Separation of Phosphoric and Arsenic acids from their salts.—The above process serves to separate phosphoric acid from the salts of those metals which can be precipitated as double oxalates decomposible by acetic acid, also from the phosphates of metals which like calcium are quantitatively precipitated by potassium oxalate. The phosphoric acid can be determined in the filtrate by precipitation with magnesium chloride also, since alcohol entirely precipitates the double ferric and the double aluminium oxalates; after addition of alcohol, the phosphoric acid separated from iron and aluminium may be determined in the filtrate. The process for estimating phosphoric acid in a mixture of the phosphates of metals of both classes is carried out as follows: The solution in hydrochloric acid is evaporated to dryness on the water-bath; potassium oxalate in solution, equal in weight to six times that of the oxides, is poured on the residue; and, after a short digestion on the water-bath, the undissolved ferric oxide is brought into solution by the addition of acetic acid; acetic acid is then added in excess, the liquid is heated, and alcohol of 95 per cent. added as long as it causes any further precipitate. The precipitate is at first bulky, but becomes crystalline and easily subsides on standing; the supernatant liquid is then perfectly colourless. After standing in a warm place for about six hours, the liquid is filtered, the precipitate washed by decantation with alcohol, and the filtrates united and evaporated to free them from alcohol and acetic acid: this evaporation is best conducted slowly in a beaker, to avoid the salts creeping over the edge. After evaporating to dryness, water is added, and any silicic acid which separates is filtered off after a time and washed with hot water; from the filtrate, after addition of ammonia which causes a dark colour to appear, the phosphoric acid is precipitated by adding magnesium chloride solution. The method is applicable when the proportion of the phosphoric acid to the oxides is very small, as in the estimation of phosphorus in cast-iron, when the following process will be found much more rapid than the molybdic acid method. The iron is dissolved in a dilute solution of bromine in hydrochloric acid, the silicic acid separated, and the filtrate evaporated to dryness. After adding the oxalate and acetic acid, the hot liquid is allowed to cool, when the greater part of the double iron salt crystallises out, the remainder being then precipitated by addition of alcohol. Arsenic acid behaves in the above respects precisely as phosphoric acid does.

In applying the method to the separation of the above metals, it must be remembered that calcium oxalate will remain undissolved by the alkaline oxalate; it may either be filtered off and washed with water containing alkaline oxalate, or since manganese if present will partially or entirely accompany the calcium, it is better to add acetic

acid and filter off calcium, magnesium, and manganese oxalates together. If ammonium oxalate has been employed to allow of the estimation of the alkalis, the precipitation of ferric and aluminium double oxalates by alcohol is impossible, since only their double potassium oxalates are thus precipitable; it is best then to evaporate the filtrate to dryness and decompose the oxalates by ignition; if the residue is then washed with hot water containing some ammonium carbonate, the alkalis are obtained in the filtrate.

The analysis of phosphorite and similar substances is performed by converting the metals in the hydrochloric acid solution into oxalates, by addition of potassium oxalate, which separates the calcium; magnesium is then precipitated by addition of acetic acid, and iron and aluminium by adding alcohol, whilst the phosphoric acid is estimated in the filtrate. The alkalis can be determined after precipitating the other metals, and their phosphates by ammonia.

If the metals are present as sulphides, they are best dissolved in nitric acid or in hydrochloric acid containing bromine, but in such cases before proceeding with the separation by the oxalate method, the sulphuric acid must be completely removed from the solution.

The oxalate method is admirably suited for rapidly and easily precipitating copper, manganese, cobalt, nickel, zinc, magnesium, and calcium, if small quantities of these metals are to be separated from a large quantity of iron. F. C.

Estimation of Silver, Chlorine, Bromine, and Iodine by Ammonium Thiocyanate. By J. Hertz (*Arch. Pharm.* [3], **14**, 322—329).—The author gives an account of Volhard's method of determining silver, &c., volumetrically by ammonium thiocyanate (this Journal, 1878, Abst., 743), and finds that it works satisfactorily. He also appends analytical data. E. W. P.

Verryken's Method of Detecting Metallic Poisons. By M. v. Wasowicz (*Arch. Pharm.* [3], **14**, 348—355).—The author most strongly recommends Verryken's method of detecting metallic poisons by combustion in oxygen (this Journal, 1874, 601), and finds that it far surpasses the Babo-Fresenius process when only small quantities are present. He, however, recommends the introduction of a manometer, for the better regulating of the current of oxygen, and the surrounding of the combustion tube with copper foil in place of tinsel. E. W. P.

Note on the Detection of some Rare Metals in Pyrites Flue-dust. By D. Playfair (*Chem. News*, **39**, 245).—The dust in question was obtained from a flue which led directly from pyrites kilns where Spanish cupreous pyrites was burned, and anything which condensed there must have done so at a very high temperature. The greater part consisted of As, Sb, Pb, Cu, and Fe, but small proportions of Tl, Te, and Se were also present. The thallium was extracted with sulphuric acid and precipitated by hydrochloric acid, and the thallium chloride reduced to the metallic state with potassium cyanide. One sample of flue-dust gave ·05 per cent., and another

·002 of thallium. Tellurium was extracted by boiling the matter insoluble in sulphuric acid in soda solution, filtering, neutralising the filtrate, saturating it with sulphurous acid, and boiling. The tellurium and selenium precipitated thereby were collected, dried, and fused with potassium cyanide in an atmosphere of coal-gas; the resulting telluride was dissolved in water, and kept in solution by passing a current of coal-gas through it. When the stream of coal-gas was stopped, the claret-coloured solution became colourless, and the tellurium was precipitated. The insoluble matter left after treatment with sulphuric acid contained ·002 per cent. tellurium and ·001 per cent. selenium. W. T.

Determination of Silicon in Pig-iron and Steel. By T. M. Drown (*Chem. News*, **40**, 40).—The author has adopted the following procedure for determining silicon in pig-iron, which, as far as his experience goes, leaves nothing to be desired.

About 1 gram of pig-iron or steel is treated in a platinum or porcelain dish with 25 c.c. of nitric acid (sp. gr. 1·2). When the action has ceased, 25 to 30 c.c. of dilute sulphuric acid (1 in 3) are added, and heat applied until the nitric acid is nearly or quite expelled. Water is then added, and the contents of the dish heated until the crystals of ferric sulphate are completely dissolved. The solution is then filtered as hot as possible, the residue washed first with hot water, then with 25 to 30 c.c. hydrochloric acid (sp. gr. 1·12), and finally with hot water. After drying and igniting, the silica will be found to be snow-white and granular.

Although the results obtained by using hydrochloric acid for the original solution of the iron show as good results as those obtained with nitric acid, the author prefers the latter on account of the silica obtained being compact and granular, whilst the use of hydrochloric acid and also of sulphuric acid alone yields a silica which is light and flaky. D. B.

Determination of Sulphur in the Ore, in the Fuel, and in the Products of the Iron Industry. By A. Rollet (*Dingl. polyt. J.*, **233**, 124).—The estimation of sulphur according to the methods hitherto in use gives good or fairly accurate results only when the substance examined contains a considerable percentage of sulphur. It is seldom that satisfactory results are obtained in the estimation of sulphur in coal and coke, and this difficulty increases as its percentage decreases; so that for its determination in cast or rolled iron or steel, the old process of dissolving in nitric acid and precipitating with a baryta salt is entirely untrustworthy, giving neither absolute nor relatively correct results.

The author claims for his process that it is quickly and easily carried out, and gives thoroughly trustworthy results. His method depends upon the conversion of the sulphur into hydrogen sulphide, and the estimation of the proportion of that gas evolved.

Rivot, Boussingault, and Eggertz have each recommended a process based on the same principle; Rivot, by acting on the iron with hydrochloric acid, and passing the liberated hydrogen sulphide through an

ammoniacal solution of cuprous chloride, and weighing the precipitated sulphide, or dissolving the precipitated sulphide in aqua regia, and weighing as $BaSO_4$. Boussingault suggested passing the gases through silver nitrate solution, igniting the sulphide produced, and weighing the silver; whilst Eggertz dissolved 0·1 gram of the metal in 2 c.c. of dilute sulphuric acid, allowing the liberated gases to impinge upon silver plates, and comparing the sizes of the spots of silver sulphide thus produced.

All these processes give wrong results, because the quantity of sulphur which is allowed to escape as hydrogen sulphide depends upon the proportions of other constituents of the sample; and of all these, carbon exercises the greatest influence; the larger the proportion of carbon the less the proportion of sulphur liberated as H_2S, part escaping in combination with hydrogen and carbon. The results obtained by Boussingault's process could not possibly be correct, because the silver nitrate would be reduced by hydrogen compounds other than hydrogen sulphide. These facts can easily be shown by making estimations of sulphur in pig-iron when drawn from the furnace on the one hand, and when at its point of greatest decarbonization, after being blown in a Bessemer steel converter, on the other. The latter sample would give three or four times more sulphur than the former, which is impossible from the fact that the pig-iron might lose, but it could not possibly gain, sulphur.

The author discovered that if the gases produced by acting on the metal with hydrochloric acid be passed through a red-hot porcelain tube along with a large excess of pure hydrogen, the compounds of carbon, hydrogen, and sulphur are decomposed, leaving the whole of the sulphur in combination as hydrogen sulphide. The author uses the silver nitrate processes of Boussingault for the ultimate determination of the hydrogen sulphide.

The old methods of estimation of sulphur in slags and ores give, as a rule, fairly accurate results. The author employs his process, however, for its estimation in coke, coal, and also in slags, by reason of its being simple, and more quickly carried out than the old process. Generally speaking it may, with some modifications, be applied to all products containing sulphur, and it has been in use at Creuzot during the last two years.

The process employed is as follows:—Hydrogen when passed over any sample in a fine state of division at a red heat combines with the sulphur which it contains: for instance, *rolled iron* is thus desulphurised in a very short time; *white pig-iron and steel* very slowly; *grey pig-iron* at first slowly, but more rapidly as the graphite changes to carbon in combination.

Ore, slag, limestone, &c., are thus partially desulphurised, the process ceasing the sooner, the more metal the substance contains whose oxides or sulphides are not decomposed by hydrogen—as lime, magnesia, alumina, and the alkalis.

The process is much hastened and any chance of sulphur being left in the substance is obviated by passing over it a mixture of 3 parts of hydrogen with 1 part of carbonic anhydride. In the case of coal or coke, this gas burns up the carbon completely, whilst in that of iron

and steel only a mere trace remains. The presence of phosphorus or arsenic, even in large quantities, does not influence the results.

When this process is to be used for the determination of sulphur in any substance rich in it, such as sulphur ore, the decomposition ought to be delayed by using less carbonic anhydride, and heating very gradually at first. If this is not attended to, a partial decomposition of the hydrogen sulphide takes place, and sulphur is deposited in the colder parts of the tube.

For the determination of sulphur in iron or steel, from 2 to 4 grams of the sample in a very fine state of division are placed in a porcelain boat, which is then pushed into the tube. The mixture of hydrogen and carbonic anhydride is passed through the tube, which is then heated to redness for 2 or $2\frac{1}{2}$ hours, and the gas passed through silver nitrate. The silver sulphide is then filtered off on a double filter, washed with hot water, and dried at 100°. The difference between the weight of the two filters gives the weight of sulphide, from which the percentage of sulphur in the sample can be calculated. The author prefers, however, to burn both filters in a porcelain or platinum tube, and from the silver found by difference, the weight of sulphur is calculated by multiplying by 0·148. The temperature at which the sample is heated should be carefully regulated, so that the substance does not cake. If this cannot be done, it should be mixed with alumina which is free from sulphur.

The author gives a number of results obtained from different samples of coal, coke, slag, and iron, in which the duplicate results obtained agree very closely with each other. He states that for most ores and slags, the admixture of 2 grams of alumina with 4 grams of the sample is sufficient, but for furnace slags and for calcareous and siliceous fluxes no mixing is required.

For coal and coke, he uses 0·5 gram mixed with 0·2 gram of alumina to prevent the caking of the ash. W. T.

Electrolytic Estimation of Mercury. By F. W. Clarke (*Amer. Jour. Sci.* [3], **16**, 200).—The slightly acid solution of the mercury salt is placed in a platinum dish, connected with the zinc pole of a six-cell Bunsen's battery, the wire from the carbon pole terminating in a thin strip of platinum foil dipping into the liquid. Mercurous compounds are first precipitated, but these soon disappear and are replaced by metallic mercury, which must be washed with water before being disconnected from the battery, then dried, and weighed. Two determinations with mercuric chloride gave respectively 73·76 and 73·85 per cent. of mercury; theory, 73·80. Even insoluble basic sulphates are rapidly decomposed in this way. Cadmium did not give good results when treated by the same process, as the metal is precipitated as a sponge, which cannot be freed from impurity. C. W. W.

Estimation of Organic Matter in Natural Waters. By G. Lechartier (*Compt. rend.*, **89**, 231—234).—When solutions of nitrates are evaporated with sulphurous acid, a certain proportion of the nitrogen is lost. The decomposition of the nitrates is, however, never complete, even with a large excess of the acid. A loss of nitrogen

also occurs when a water containing carbonates and ammoniacal salts is evaporated to dryness, and hence it is necessary to remove the carbonates before evaporation. The author prefers to determine the nitrogen existing as ammoniacal salts by boiling with magnesia, which gives accurate results and does not affect the organic matter. He then determines the total nitrogen existing as nitrates and organic matter, and the estimation of the nitrogen present as nitric acid gives the amount of organic nitrogen by difference. A separate experiment is required for the estimation of the carbon. C. H. B.

Detection of Blighted Wheat in Flour by the Spectroscope.—By J. Petri (*Zeitschr. Anal. Chem.*, 1879, 211—220).—The methods hitherto described for detecting blighted corn in flour lack certainty, and fail to detect a small percentage. Blighted corn by itself is very easy to recognise; the microscope reveals small oval bodies, with usually two nuclei, in great numbers; they exist on the exterior layer of the grain. In the middle layers the darker particles are seen, which give blighted corn its dark violet appearance; there are also seen the oil-cells and drops of oil of varying size. If the flour made from blighted corn is extracted with alcohol, the fat and resin are removed, together with a brownish colouring matter; when a few drops of dilute hydrochloric or sulphuric acid are added to the violet-grey residue, the colour changes to a fine red. This red substance is easily soluble in cold alcohol, ether, amyl alcohol, benzene, and chloroform, and its spectroscopic behaviour serves to identify it. Its solutions obtained as above, when strong, or in thick layers, transmit only red light; on gradual dilution, yellow first appears, then a part of the green, and at last the whole spectrum appears, with the exception of two absorption-bands, which are visible even after extreme dilution, and are extremely characteristic. One band lies in the green near E, the broader and stronger band lies in the blue, between F and G. On comparing the spectrum with that shown by rosaniline, the band near E is seen to commence at the left side of the characteristic rosaniline absorption-band, when the red end of the spectrum lies to the right of the observer. These bands are seen with less intensity in the brown extract of the flour. The red colouring substance is soluble in water and in dilute alcohol, but is taken from these solvents when the solutions are shaken with ether, amyl alcohol, chloroform, benzene, &c.; in all these solutions the two absorption-bands are seen, although slightly displaced, but they are most distinctly seen in the ether solution. Alkalis change the red colour to yellow. It is easy to show that the methods hitherto in use are insufficient to prove the presence of blighted corn; the development of a smell of trimethylamine, on heating with potassium hydrate solution, is not peculiar to blighted corn; any gummy substance which is undergoing decomposition, or has been kept in a moist condition, gives off the smell, either with or without potash; further, the yellow colour shown by the dough made with potash solution is seen more or less with all flour, and is very evident when the flour is somewhat spoilt. Jacoby's method is the most trustworthy process hitherto described; the flour is extracted with boiling alcohol as long as any colouring matter is removed; the flour,

after having been dried by pressure, is then mixed with more alcohol, and with a few drops of dilute sulphuric acid. The appearance of the red colour serves to detect blighted wheat, and the intensity of the colour, by comparison against standard tints, serves to determine the quantity. Some flour free from blighted wheat, gives a slight red colour by this process, but such a solution does not give up its colouring matter when shaken with amyl alcohol, and the colour does not give the above absorption spectrum. The process described below is essentially that of Jacoby, but the author introduces the confirmatory tests already referred to. About 20 grams of the flour are boiled with alcohol on the sand-bath for about five minutes, the liquid being constantly stirred, and the alcohol replaced as it evaporates. After settling, the alcohol is poured off, and this treatment repeated until the alcohol is no longer coloured; 20 drops of cold dilute sulphuric acid are then added and well stirred, and after standing for a time the liquid is decanted through a filter, and examined by the spectroscope in thick or thin layers, according to its depth of colour. About a quarter of a test tube of the liquid is then mixed with about twice its volume of water, and the milky liquid is shaken with about 2 c.c. of amyl alcohol; another portion is similarly shaken with chloroform; another with benzene; and a fourth with ether. If the original liquid was red, and imparted a red colour to each of the four solvents, and if all of these solutions show the characteristic absorption spectrum, the presence of blighted wheat is proved. The quantity present may be estimated by comparison against a solution similarly prepared from blighted corn flour. Ether may be used instead of alcohol for extracting the disturbing colouring matter from the flour, the ether is then well shaken with the flour without being heated. Pure flour was mixed with blighted corn flour, and it was found that when 20 grams were used an adulteration of 2 per cent. could be detected: for the detection of smaller percentages, larger quantities of flour had to be employed. The spectroscopic method for quantitative purposes has not yet been tried, but since all samples of blighted corn do not contain equal quantities of the colouring substance, it is of doubtful applicability; by proceeding in the following way, however, the percentage of blighted corn was estimated with fair accuracy in artificial mixtures of pure and blighted flour. After removing the yellow colouring matter from 20 grams of flour by treatment with alcohol, the residue was mixed with 20 drops of dilute sulphuric acid and 30 c.c. of alcohol, and allowed to digest for a quarter of an hour at a gentle heat; this liquid was decanted through the filter used for the alcoholic extracts, and the residue, after digestion with 30 c.c. more alcohol, was thrown upon the filter, and after being allowed to drain was washed with warm alcohol, until all the filtrate together measured about 100 c.c.; the last portions were usually colourless, if not a larger quantity of alcohol was used, and the whole volume used was noted down. A comparison solution was meanwhile prepared in exactly the same way from 1 gram of blighted corn; and the colorimetric process was carried out by pouring the liquids into two similar graduated cylinders, with taps at the side, and lessening the depth of the more strongly coloured liquid, until the intensity appeared the

same in both. In extracting the colour, the quantity of alcohol used must be limited, as the red colouring matter is very unstable in acid solution, and therefore concentration is impossible. It is very difficult to detect fragments of blighted corn by the microscope, unless the flour has first been stirred with water, to which a few drops of solution of iodine in potassium iodide solution have been added; after standing for a time the starch granules of the pure flour become blue, and the yellowish flour from the blighted corn can then be picked out under the microscope. Working with a larger spectroscope, the author detected three absorption-bands instead of two, and found that these bands corresponded very nearly with bands 4, 5, and 6 of a solution of chlorophyll in ether. Measurements of the amount of absorption shown by these bands and of their precise position in the spectrum are given; the middle of each band showed the greatest absorption, and the position of these middle portions correspond with wave-lengths 536·4, 497·5, and 465·6 respectively. On dilution the first band faded first, then the third, and the second last. F. C.

Estimation of Starch in Sausages. By L. Medicus and E. Schwab (*Deut. Chem. Ges. Ber.*, **12**, 1285—1286).—A slice of the sausage when moistened with dilute iodine solution, and examined with a magnifying glass, shows the starch granules coloured blue if starch is present. To estimate it, a portion of the sausage is digested at 30—40° for two hours with a known quantity of diastase solution, made by digesting malt with water, and then the solution is allowed to stand for about 18 hours at the ordinary temperature. The mass is then filtered and well washed, the filtrate boiled and filtered from the coagulated albumin. The filtrate is then boiled with dilute hydrochloric acid, to convert the maltose and dextrine into grape-sugar, which is estimated by Fehling's solution. The grape-sugar yielded by the malt extract used is also determined; this deducted from the amount obtained gives the grape-sugar formed from the starch; thus as much as 84·6 per cent. of starch added may be estimated. The authors recommend a deduction of 1 per cent. as representing the starch in the pepper. P. P. B.

Weselsky's Reaction for Phloroglucin. By H. R. Procter (*Chem. News*, **39**, 245).—This reaction consists in the production of a cinnabar-red precipitate, when a trace of phloroglucin is added to a solution of aniline nitrate, or to toluidine containing a little nitrite, on standing some hours.

Many tannins on being heated with dilute sulphuric acid, are resolved into glucose and peculiar red bodies, called "phlobaphenes," which, when fused with potassium hydrate, are decomposed into protocatechuic acid, and another body, which is a fatty acid or phloroglucin, according to the sort of tannin employed.

To try to recognise the phloroglucin-tannins, the author applied Weselsky's reaction directly by mixing in test-tubes 5 c.c. H_2O, 1 c.c. of a saturated solution of aniline nitrate, and 1 c.c. of a very dilute solution of potassium nitrite, and adding to each tube 1 c.c. of solutions of the following bodies (containing about 5 grams per litre of

the tannins) :—(1) Gallic acid; (2) Gallotannic acid; (3) Pyrogallol; (4) Gambier; (5) Oak bark tannin; (6) Chureo tannin; and, for the sake of comparison, (7) Cane-sugar; and (8) Impure grape-sugar.

After five minutes the first three solutions had changed to pale-yellow, the second three to deep yellow, whilst 7 and 8 remained colourless.

After one hour, 1 and 2 had changed to orange, but gave no precipitate, but after twelve hours a dark red-brown precipitate had formed. No. 3 changed to a turbid orange colour after one hour, and threw down a reddish-brown precipitate after twelve hours.

The solutions of Nos. 4, 5, and 6 had changed to orange colour after one hour; 4 was turbid; whilst 5 and 6 contained a red precipitate. After twelve hours each had thrown down a red precipitate; whilst 7 and 8 gave yellow liquids after one hour, and traces of a brown precipitate after twelve hours.

Nos. 4, 5, and 6 are bodies known or supposed to contain phloroglucides, and they give the red precipitate, but other bodies give precipitates approaching in colour to the red.

The author has made preliminary tests as to the application of Wiesner's test as a means of detecting the presence of phloroglucin. The test consists in moistening a deal-shaving with a solution of phloroglucin, and then with hydrochloric acid, when a purple coloration is produced (*ibid.*, 1878, 809). Gambier solution gives it strongly. W. T.

Determination of Free Acid in Tan-liquors. By H. R. Procter (*Chem. News*, **39**, 248).—Tan-liquors usually contain in addition to tannins, gallic acid, and catechu, also acetic and fatty acids, and frequently free sulphuric and hydrochloric acid. It is advisable to know which acids are capable of dissolving the lime and swelling the tissue of the hide. Litmus and alkaline solutions cannot be used, owing to the colour of the tan-liquors. The author uses a standard solution of lime-water, which he adds to the filtered liquor in a beaker, until the solution becomes turbid by the precipitation of tannate of lime, which indicates that all the other acids have been neutralised. This finishing point, he states, can be easily seen by holding the beaker over a printed page. W. T.

Estimation of Acetic Acid in Wine. By L. Weigert (*Zeitschr. Anal. Chem.*, 1879, 207—211).—The separation of acetic acid from wine by distillation is incomplete. Even when phosphoric acid is added to raise the boiling point, and the distillation is several times repeated after addition of distilled water, as has been proposed by Kissel, the whole acetic acid present and not only that in the free state is estimated, and the process becomes very troublesome and tedious, each estimation taking from 4 to 6 hours for its execution. The author first tried titrating the acid in the wine itself, and then titrating the acid in the dry residue left on evaporation, hoping thus to get the volatile acetic acid by difference, but the results were very unsatisfactory. A satisfactory method both as regards accuracy and rapidity of execution, however, depends on lowering the boiling point

and hastening the evaporation by reducing the pressure upon the surface of the liquid. The estimation is carried out as follows:—A long-necked flask of about 250 c.c. capacity, and containing 50 c.c. of the wine is connected with a condenser, the tube of which passes through one hole in a doubly-bored cork, closing a strong cylinder, a tube which passes through the other hole in the cork serving to place the whole air-tight apparatus in connection with a Bunsen's or other water-pump. The flask is heated in a water-bath containing a saturated solution of sodium chloride. The pressure is reduced to about 500 m.m., and the further action of the pump is then unnecessary during the distillation; in a few minutes the whole of the liquid has passed over. The cylinder is then disconnected slowly to avoid too violent an inrush of air; the distillate is poured into a vessel for titration, and after the wine residue in the flask has been made up to its original volume by addition of distilled water, the distillation is repeated. This process of redistillation is to be performed in all four times, and it is unnecessary each time to rinse out the condenser tube or to collect very carefully the last few drops of each distillate, since very little acid comes over in the last portions. It is well not to use thick india-rubber tubing for connecting the apparatus with the pump, as the ordinary tubing by collapsing serves to moderate the rush of air into the flask. It is found that the fourth and fifth distillates contain almost the same quantity of acid; hence no appreciable error is introduced, if the first three distillates are titrated as soon as they are ready, and to the quantity of acid thus found double that found in the fourth is added; the process can thus be carried out in less than three-quarters of an hour. Duplicate estimations showed that the differences lie within the error ordinarily incurred in titrating acetic acid; also, after adding a known quantity of acetic acid to the same wine, it was correctly estimated after deducting the acetic acid previously found in the wine. F. C.

Detection of Free Tartaric Acid, and of Sulphuric Acid, in Wine. By J. Nessler (*Zeitschr. Anal. Chem.*, 1879, 230—239).—The author answers the criticisms of Claus on an opinion given by him as to the trustworthiness of the chemical proof of the presence of free tartaric acid and sulphuric acid in wine (*Zeitschr.*, 1878, 314). The author still maintains that tartaric acid, if present, cannot be extracted from wine by agitation with ether, because it is almost insoluble in ether; in a direct experiment, only 3·93 per cent. of the tartaric acid present was removed by ether; a larger proportion is dissolved if the wine be evaporated to a syrupy consistence, since the presence of water tends to hinder the solution, but even in this case only 25 per cent. of the acid was removed by ether. The presence of alcohol increases the solubility considerably, and employment of ether containing alcohol will therefore yield different results. The author details numerous experiments to establish the trustworthiness of his method for the detection of free tartaric acid in wine; the method consists in shaking the wine with powdered tartar for some time, filtering and adding some concentrated potassium acetate solution and noticing whether tartar crystals form. An opinion as to the quantity

of free tartaric present may also be formed by the length of time elapsing before the crystals appear. It was found that no separation of the tartar crystals occurred unless the acetate was added. The crystals formed most readily when the liquid was kept at constant temperature, and cooling should be avoided, as it might cause the separation of tartar crystals originally present in the wine. By allowing the liquid to stand for 24 hours, 1 per cent. of free tartaric acid was detected in a liquid free from other organic acids, and in wine or a liquid containing organic acids only, evaporated to one-half, it was possible to detect 0·05 per cent.; the presence of less free acid than is thus detectible would not prove the addition of tartaric acid to the wine. It is well to divide the liquid, after agitation with tartar and filtration, into two parts, and to add the acetate to only one portion; any separation of tartar originally in solution will then be detected in the blank portion. Out of 30 artificial wines, free tartaric acid was detected in 25 by this means without evaporation. A few drops only of concentrated acetate solution should be added, as the addition of excess hinders the formation of tartar crystals; the presence of other organic acids assists the separation of the tartar. No opinion as to the presence of free tartaric acid can be formed by estimating the total acidity of the wine and its ash, since the acidity is mainly due to other acids. The presence of sulphates in a wine does not necessarily prove the addition to it of sulphuric acid, since sulphates may be taken up from the soil or manure, or from the gypsum with which the grapes are sprinkled in the South of France, in Spain, and in Greece. Analyses of 38 genuine French red wines showed quantities of sulphuric acid ranging from 109—328 centigrams per litre; hence the presence of 201 centigrams, the quantity found by Claus, does not prove adulteration. The feeble alkalinity of the ash and the presence in it of but little calcium also cannot be considered as proofs of the addition of sulphuric acid; since when alcohol is added to a saturated aqueous solution of gypsum and tartar, a mere trace of calcium remains dissolved, potassium sulphate being left in solution. Hence, if gypsum were present in the must, or had been subsequently added, the production of alcohol during the fermentation would lead to the formation of potassium sulphate, and the wine would yield an ash, therefore giving only feebly alkaline reaction, and almost free from calcium. A direct test for free sulphuric acid, or acid potassium sulphate, consists in letting a strip of filter-paper hang with one end in the wine for several hours, after which the paper is dried and heated at 100°; the part moistened by the wine darkens in colour and becomes brittle. This test detects even 0·02—0·04 per cent. of free sulphuric acid in a liquid to which sufficient sugar has been added. The author concludes, that if 5 grams of wine ash contain 3·57 grams of potassium sulphate, and the wine contains but little calcium, no alumina, and a little free tartaric acid, it must not be concluded that sulphuric acid has been added. F. C.

On the Iodosulphates of the Quinine Alkaloïds. By B. W. Dwars (*Arch. Pharm.* [3], **14**, 329). — The great insolubility of quinine iodosulphate is employed as a test for the purity of quinine

salts in the following manner:—In every 10 c.c. alcohol of 92 per cent., to which has been added a drop of dilute sulphuric acid and two drops iodine tincture, is to be dissolved, of the sulphate, 50 mgrams., of the hydrochloride, 45 mgrams., of the citrate, 65 mgrams., and of quinine, 43 mgrams.; immediately on the addition of these salts, a precipitate is formed. The other alkaloïds require more iodine and a more concentrated solution: they are at first redissolved, but when a large excess of iodine is present, they are precipitated in the following order: cinchonidine, quinidine, cinchonine. E. W. P.

A New Method of Testing Butter for Foreign Fats. By J. Koettstorfer (*Zeitschr. Anal. Chem.*, 1879, 199—207).—The investigations by Hehner's method prove that butter contains a larger proportion of fatty acids with not more than ten atoms of carbon in their molecule than was previously assumed; and since the molecules of most other fatty substances contain a greater amount of carbon atoms, it is evident that a given weight of butter must comprise a greater number of molecules than an equal weight of any of these other fats. Hence on determining the amount of potassium hydrate necessary for saponifying a given weight of different fatty substances, butter is found to require more standard alkali than the fats used for its adulteration. This method of titrating all the fatty acids present is preferable to Hehner's, on account of its greater simplicity and rapidity of execution, half an hour sufficing for the execution of an analysis when the standard solutions are in readiness. The standard solutions employed are a deci-normal hydrochloric acid, and potassium hydrate dissolved in highly rectified spirit to about the same strength. As an indicator, a measured quantity of very dilute alcoholic solution of phenol-phthaleïn is added. The process is carried out as follows:—After purifying the fat by repeated fusion and filtration, from 1 to 2 grams of it are weighed into a tall beaker, of about 70 c.c. capacity; 25 c.c. of the titrated potassium hydrate solution is added, and the beaker is heated in a water-bath. When the spirit is nearly boiling, the contents are stirred for a minute with a glass rod to cause the fat to dissolve. The rod is rinsed with spirit into the beaker and laid carefully aside, the beaker meanwhile being covered with a watch-glass, and heated short of violent ebullition for a quarter of an hour. The watch-glass is then rinsed with alcohol into the beaker, and the contents once more stirred with the glass rod for a minute to saponify any particles of fat still adhering to the rod. After removing the beaker from the water-bath, 1 c.c. of the phenol-phthaleïn solution is added, and the excess of alkali titrated with the standard acid; the change of colour to pure yellow sharply indicates the end of the reaction.

Heating for 5 minutes only, as recommended by Hehner, is not always sufficient to complete the saponification. The strength of the alkali solution should be fixed by titration with the standard acid, after 25 c.c. have been heated as in the above process for 15 minutes, since a slight oxidation of the spirit occurs during the heating which somewhat lessens its titre, about 0·1 c.c. less of acid being required by the 25 c.c.; the alkali solution suffers about an equal alteration by

standing five or six days at ordinary temperatures; hence it must be controlled from time to time. Standard sulphuric acid cannot be used, since the potassium sulphate formed during the titration is insoluble in alcohol, and the separated crystals interfere with the accurate observation of the final reaction. The author expresses the quantity of potassium hydrate required for 1 gram of fat in milligrams, since the number thus used was found to be constant in repeated analyses. The number of milligrams of potassium hydrate neutralised by 1 gram of butter was found to vary in different samples between 221·5 and 232·4, giving a difference of 10·9. The fats used for adulterating butter and for making artificial butter gave lower numbers. Stearin gives by calculation 188·8, oleïn, 190·0, and palmitin, 208·0; and since these are the principal constituents of the fats, it would be anticipated that the results given by them in the new process must be lower than that yielded by butter. The numbers yielded by beef suet, tallow, lard, and mutton suet varied between 195·4 and 197; whilst for olive oil, 191·8, and for rapeseed oil, 178·7 were the results. The difference between the highest of these numbers and that for butter is sufficient to allow of an approximate calculation of the percentage of adulteration. From an artificial butter consisting almost entirely of oleo-margarin, it was calculated that the number for pure oleo-margarin would be 195·5, and since lard yields almost the same number, and oleo-margarin and lard are the most common adulterants of butter, 195·5 may be taken as the number to form the basis for calculation of adulteration. Since the numbers for pure butter vary between 221·5 and 232·4, a butter which yielded a number not lower than 221·5 must be considered to be unadulterated. If the number is lower than 221·5, the percentage of adulteration is estimated from the equation $x = (227-n)\ 3{\cdot}17$, in which x is the percentage required, n the number obtained for the sample analysed, and 227 is the mean number for pure butter. Owing to the variations exhibited by pure butter, an error of 10 per cent. in the calculation of percentage adulteration is possible; and assuming that butter of 232·4 has been adulterated down to 221·5, 29 per cent. of foreign fats may be introduced and remain undetected. By Hehner's method, however, as much as 40 per cent. may escape detection. This process of quantitative saponification may be probably employed to distinguish between different fats and oils, and to detect adulteration of one oil or fat by addition of another.

F. C.

Analysis of Turkey-red Oil. By G. Stein (*Deut. Chem. Ges. Ber.*, **12**, 1174—1175).—As is well known, Turkey-red oil (ammonium sulphoricinoleate and ammonium sulphopyroterebate) may be mixed with large quantities of water without undergoing any visible change.

In order to determine the weight of oil in such a mixture, 10 grams are weighed out into a porcelain basin, together with 25 grams of dry wax, and 75 c.c. of a cold saturated solution of common salt, and the whole heated on a water-bath. The Turkey-red oil being insoluble in a solution of salt, separates out on the surface of the liquid, and dissolves in the fused wax. The resolidified cake of the latter is then freed from attached salt by means of filter-paper, dried over sulphuric acid, and weighed. This weight, minus that of the wax taken, gives

the weight of Turkey-red oil in the original mixture of oil and water. The amount of oil in various commercial samples from different sources varied between 61·4 per cent. and 77·5 per cent. T. C.

Estimation of Urea. By C. Mehu (*Compt. rend.*, **89**, 175).—It is well known that when urea is acted on by hypobromites, 8 per cent. of the nitrogen is not disengaged. The author finds that by mixing the solution of urea with glucose or cane-sugar before adding the hypobromite, the whole of the nitrogen is evolved. The presence of an excess of sugar does not impair the accuracy of the results.

C. H. B.

Technical Chemistry.

Softening Magnesia-hard Water. By J. Grossman (*Chem. News*, **39**, 258).—The author has made experiments on the large scale with a view to soften magnesia-hard water by Clark's process, and he finds that by it magnesium carbonate is precipitated as completely and as easily as calcium carbonate. The water in question was pumped from a colliery 96½ yards deep at Collin's Green, near St. Helen's, and the author gives the percentage of CaO and MgO contained in the different strata through which the well passed: they contain from 0·22 to 0·52 per cent. MgO. The hardness of the water was principally temporary. He confirms the statement, that mere boiling does not make much difference in the hardness of a water. Collin's Green water (the hardness of which is almost entirely temporary) when boiled for five minutes was only reduced from 27·8° to 17·6°. The author made two sets of experiments, one by using lime-water, and the other milk of lime. 2·67 lbs. of lime containing 90 per cent. CaO were added to each 1,000 gallons of water. *The total hardness* by the process was reduced from 23·3° to about 5·4°, *the total solid matter* from about 33·8 to about 13 grains per gallon, and the lime from 9·13 to 1·62, and the magnesia from 5·23 to 0·23 grains per gallon.

The precipitation was effected much more easily with lime-water than with milk of lime; in both cases the precipitate settled, and the softened water was left quite clear in from 3 to 5 hours.

Wanklyn states that 1 equivalent of MgO takes as much soap solution as 1½ equivalents of CaO; under those circumstances Collin's Green water should have shown a hardness of 35·9° instead of 23·3°. Magnesia-hard water requires *less* soap solution than the same equivalent of lime-hard water, but the results given by Clark's soap solution standard in magnesia-hard water cannot be relied upon in any way.

W. T.

Sanitary Notes on Potable Water. By G. Bischof (*Sanitary Record*, May, 1879). — The author criticises Lewin's paper (this vol., p. 343). He contends that Lewin attempted to purify urine by the use of the spongy iron filter, whereas that filter is intended for

the treatment of impure waters; he objects also to the rapidity with which Lewin's solutions were run through the filter, and holds that Lewin's methods of analysis were faulty and his general procedure inexact.

Experiments are detailed in which water before and after filtration through spongy iron was allowed to act on pieces of fresh meat, and the conclusion is drawn that water which has been efficiently filtered possesses considerable antiseptic properties.

M. M. P. M.

Experiments with Animal Charcoal, Silicated Carbon, and Spongy Iron Filters. By F. De Chaumont (*Army Medical Report*, 1877, 170—171).—These experiments deserve consideration in connection with the results of experiments made by Wigner (this vol., p. 493).

Animal charcoal in pieces, in a moderately compressed state, allows water to pass rapidly, and provided the charcoal is frequently renewed or reburnt, exerts a useful purifying action on water which is to be used at once. Such water, however, when stored, soon shows evidence of low forms of life, and yields after a time a sediment of organisms: this takes place even when analysis immediately after filtration shows no albuminoïd ammonia. This is probably due to germs passing the charcoal undestroyed, and being furnished with the requisite pabulum by the phosphates which the water dissolves from the charcoal. It is known also that although decomposing albumin is arrested by the charcoal, fresh albumin passes unchanged. After such charcoal has been in use for some time, it becomes charged with the impurities which it has removed from the water, and yields these impurities again to water which stands in contact with it: hence a filter kept immersed in a cistern may ultimately contaminate instead of purifying the water.

Silicated carbon, and other forms of consolidated carbon, present little advantage in the above respects over loose pieces of charcoal, and have the disadvantage of being easily clogged and less easily removed and purified; with neither form of charcoal is lengthened contact with the water desirable, nor should the filtered water be allowed to stand for any considerable time before being used.

Spongy iron is found to be a very powerful filtering substance: used in conjunction with "prepared sand," consisting of gravel and pyrolusite, which removes a trace of iron taken up by the water, a contact of twenty-two minutes will purify all but very impure waters. Its purifying action, moreover, is complete; and it was found that water filtered through these substances could be stored without any change or development of life occurring; and further, that water left in contact with the filtering medium for an indefinite period was in no way contaminated.

F. C.

Purification of Gas by Ammonia. By W. Göbel (*Dingl. polyt. J.*, **232**, 180—182).—The author passes ammonia into the crude gas, and cools the mixture by means of condensers. The gas is then introduced into the bottom of a coke-scrubber, ammonia gas being added simultaneously at a temperature of 25 to 40°. A con-

stant fall of water containing gypsum passes through the scrubber, the water having a temperature of 19°. Carbonic acid, sulphuretted hydrogen, cyanogen, and bisulphide of carbon are removed by this treatment. Gas thus purified no longer requires purification with lime or iron, a circumstance which is of great importance in gas making, inasmuch as thereby the difficulties of charging and emptying the purifiers are not only removed but also all nuisances arising therefrom stopped; moreover, a bye-product is consumed, which hitherto has been useless in many gas works. D. B.

Decomposition of Bones by Steam. By D. König (*Bied. Centr.*, **8**, 69).—By subjecting bone-meal to the action of steam, the nitrogen is rendered more easily convertible into ammonia.

After 21 weeks, 38·62 per cent. of the nitrogen in the steamed bone-meal, and 24·30 per cent. in the same unsteamed had become converted into ammonia. A. J. C.

Retrogradation of Superphosphates. By H. Joulie (*Compt. rend.*, **88**, 1324).—In the presence of an excess of acid, superphosphates undergo no change, but if the quantity of acid is insufficient for complete decomposition, the action of the sesquioxides present on the calcium phosphates gives rise on drying to phosphates of iron and aluminium, together with tricalcium phosphate. The addition of chalk, or of plaster containing calcium carbonate, produces the same effect. C. H. B.

Green Pigment from Barium Chromate. By T. Douglas (*Chem. News*, **40**, 59).—Barium chromate, which is precipitated on the addition of a solution of barium chloride to a solution of a soluble chromate, is used to some extent as a pigment under the name of "lemon yellow." When strong sulphuric acid is added to this substance in the dry state, great heat is developed, and it is coloured a deep red from the liberation of chromic acid. If the mixture be now ground up in a mortar and heated to bright redness, the chromic acid is reduced to sesquioxide, which colours the mass green, yielding a pigment possessing considerable body.

From the great heat developed, it might be rather dangerous to mix the dried chromate with strong sulphuric acid on a large scale. The better method of proceeding would probably be to mix the wet precipitate with acid of ordinary strength, and dry the mixture at a moderate heat. The chromic acid would then be thoroughly incorporated with the other substances. D. B.

Solvay's Soda used in the Preparation of Ultramarine. By O. Ilgen (*Dingl. polyt. J.*, **232**, 177—180).—It is stated that large quantities of soda are now prepared by Solvay's ammonia process, the product obtained being of great purity. Owing to the latter circumstance, and the fine granular structure of this soda, ultramarine manufacturers have rejected its use, as they found that the mass fused together very readily, and thus prevented the formation of blue. How-

ever, this difficulty may be entirely removed by adding sodium sulphate to the mixings. The author has used Solvay's soda for several years on a large scale, and has been able to produce any kind of shade with it. The quantity of sulphate added is equal to about one fourth the weight of the soda used. Solvay's soda may not only be recommended on account of its regular composition, but also on account of its cheapness and high percentage of carbonate. The following are the average results of some analyses:—

	Na_2CO_3.	K_2SO_4.	NaCl.	Moisture.	Insoluble.
Solvay.....	99·63	0·00	0·06	0·15	0·16 = 100·00
Kuhlmann	95·80	2·50	0·50	0·70	0·50 = 100·00

The author also recommends the use of Solvay's pure calcium chloride for precipitating the washed ultramarine which no longer deposits in pure water. D. B.

Contributions to our Knowledge of Clays. (*Dingl. polyt. J.*, **232**, 159—165).—In examining clays, Lindhorst dissolves the residue insoluble in sulphuric acid with hydrofluoric acid, separates the constituents, and calls the remainder silicic acid.

According to Senft, clays are still being formed at places where felspar rock is decomposed by weathering, but the greater part of the massive deposits of clay, loam, and marl have originated principally in the decomposition of conglomerates, sand-stone, roof-slate, marl and lime, water having washed them to their present beds. The fatty clays are found in the deepest parts of former inland lakes, the "flookans" at the banks of meers, the loam deposits in open bays situated in the vicinity of former valleys of rivers or seas, the "loess" deposits in bays situated some distance from such valleys, the marls in the deep creeks of former lakes in lime-rock regions. Senft distinguishes three varieties:—

1. Kaolin or porcelain earth perfectly free from iron, adheres slightly to the tongue, is infusible and non-vitrifiable, but shrinks together and becomes hard when heated.

2. Fuller's earth or pipe-clay contains as much as 9 per cent. ferric hydrate, 10 to 12 per cent. excess of silicic acid, and 1·25 per cent. magnesia. Adheres strongly to the tongue, feels greasy, and is almost infusible.

3. Common clay or potter's clay, mixed intimately with at least 10 per cent. ferric oxide, adheres strongly to the tongue, is fusible and vitrifiable, but splits to pieces when heated in the presence of much sand or lime.

Senft gives some tables relating to the substances which may accompany common clay, and according to the constitution of the admixtures he distinguishes two varieties, viz., clays free from lime, and clays containing lime.

Smock has analysed a number of clays from New Jersey, which are remarkable, owing to the high percentage of titanium present:—

	SiO_2.	Al_2O_3.	H_2O combined.	K_2O.	Na_2O.	CaO.
I.	31·32	27·13	9·63	traces	traces	traces
II.	43·22	38·94	13·71	0·30	0·17	0·15
III.	28·21	19·88	6·02	1·66	0·33	0·11
IV.	16·79	17·52	5·17	0·14	0·21	—

	MgO.	FeO_3.	TiO_2.	Quartz.
I.	0·08	1·26	1·93	29·00
II.	0·11	0·81	1·35	1·31
III.	0·37	1·51	1·02	41·30
IV.	0·25	0·65	0·90	58·15

Hauenschild mentions the presence of vanadium sulphate in the yellow and red facings of the public buildings recently erected in Vienna.

According to Olschewsky the resistance which tiles offer to the weather depends on their porosity, and the latter on the constitution of the clay and the temperature of burning. From another source this statement is disputed; the porosity is said to be no criterion for judging as to the resistance offered to the weather, since Swedish tiles are often destroyed in a short time by the influence of the atmosphere. D. B.

Liquid Cyanides and Chlorides in Blast Furnaces. (*Dingl. polyt. J.*, **232**, 186).—The charcoal-furnace at Alsó-Sajó, in Hungary, is charged with spathic iron and brown-iron ore, and produces alternately specular iron and white pig iron. The furnace has two tuyere holes 92 mm. in diameter, and a blowing pressure of 33 mm.; the blast temperature is 400° to 450°, its weekly production 80 tons with a consumption of 70 kilos. of coals per 100 kilos. of iron.

This furnace, especially when worked for ordinary white pig iron, *i.e.*, at a comparatively low temperature, frequently shows liquid saline masses, which escape through the tapping hole, immediately previous to the letting off of the slag. These masses are distinguished by the large amount of white smoke evolved from them. The liquid slag also gives off a similar smoke. The solidified saline mass was coloured bluish-grey, is readily soluble in water, strongly alkaline, and smells of prussic acid. Its composition is as follows:—

K.	Na.	Fe.	CN.	Cl.	SiO_2.	SO_3.	Insoluble substances.	Moisture.	CO_2 and loss.
19·40	0·25	6·34	7·25	8·65	0·52	0·06	42·08	1·52	13·93

The chlorine appears to be in combination with potassium, the cyanogen with iron, and the excess (if any) with potassium, so that the mass is a compound of potassium chloride and cyanide, iron cyanide, potassium carbonate, sulphate, and silicate. The formula for the cyanogen and chlorine compounds is $K_2Fe(CN,Cl)_2$. D. B.

Obtaining Vanadium from the Uranium Ore of Joachimsthal. By A. Patera (*Dingl. polyt. J.*, **231**, 556—557).

Refining Copper. By H. Hesse (*Dingl. polyt. J.*, **232**, 187).—

The author melts refined copper in a reverberatory furnace under a layer of charcoal, and overpoles it so as to completely remove all the cuprous oxide. The melted copper is then poured into a clay mould and covered with a lid, through which carbonic anhydride is introduced until the mass is quite cold. The gases absorbed by the copper, especially sulphurous acid, are said to be expelled by this treatment, whilst the resulting copper is distinguished by extraordinary softness, toughness, and firmness. D. B.

Behaviour of Tin and Lead Alloys with Vinegar. By R. Weber (*Dingl. polyt. J.*, **232**, 153—159, and 264—273).—The author undertook a complete series of experiments regarding the action of vinegar on vessels made of plumbiferous tin in order to obtain certain data, which may be of some use both in a sanitary and commercial point of view.

The trials were made partly with alloys of tin and lead, and partly with mixtures of tin, lead, and antimony. The vessels were dried at a moderate temperature, weighed, and treated with commercial vinegar containing 6·17 per cent. acetic anhydride. To determine the metallic oxides, which were partly in suspension and partly in solution, the vinegar was treated with nitric acid and evaporated: the residue was dried on a water-bath, moistened with nitric acid, boiled out with water, ignited and weighed. The lead in the oxide of tin obtained was separated in the usual manner.

The results show that the quantities of dissolved metal decrease in rapid progression as the amount of tin in the alloy increases. Although in treating the vessels a second time with vinegar less metal is dissolved, the proportion of tin in the vinegar is larger. This circumstance is explained by the separation of part of the dissolved lead caused by the action of the alloy on the metalliferous vinegar. Vessels, therefore, give up larger quantities of metal, when first used. The same condition applies also to newly-cleaned vessels.

In the next place, the action of vinegar on vessels made of an alloy of lead and tin containing 4 per cent. of antimony was tried. The results were similar to the above, the solubility of lead decreasing rapidly as the quantity of tin increases. According to the author's views, the addition of antimony, which increases the rigidity of tin vessels, is not injurious from a sanitary point of view.

In the above experiments, air always had access; this causes the oxidation of the metal which is favoured by the vinegar. This circumstance has been proved by actual experiment.

The precipitation of lead from the metalliferous vinegar by the alloy forms an important factor in explaining the reactions in question. Fleischl disputes the possibility of precipitating lead by means of tin. The author therefore considered it necessary to investigate this reaction. His observations coincide with those of Proust, Klaproth, and Hermbstedt, who do not doubt that lead is precipitable by tin.

Vessels made of an alloy of silver and copper gave similar results when treated with vinegar, hence, judging from a sanitary point of view, the quantity of lead in tin vessels may be equal to that of copper in silver vessels. D. B.

Detection of Fire Damp. By R. A. Smith (*Chem. News*, **39**, 267).—For this purpose, the author employs a compression syringe made by taking a piece of strong glass tube open at both ends, 2 inches long and 8 mm. internal diameter. Slipping a piece of india-rubber tubing over it to act as packing, and pushing both into a brass tube closed at one end, with the bottom and sides well covered with glue, which was found to make the best air-tight joint, and yet not to be ignited by the heat developed by the compression. A hole is cut out of the brass and caoutchouc tube exposing the glass under it to act as a window, and the small brass tube or cap containing the glass tube is screwed on to a longer brass tube of precisely the same diameter as the glass tube, and in which a brass piston well packed and lubricated with soap is fitted. A mixture of air with 5 per cent. of marsh-gas flashes when the piston is driven down rapidly by a blow with the palm of the hand.

The apparatus is made still more delicate by placing a small piece of platinum-black at the bottom, so that by its aid $2\frac{1}{2}$ per cent. of marsh-gas can be detected. In using this apparatus, any person can walk in the dark along the workings of the pit, and by forcing down the piston of the apparatus from time to time observe through the window at the bottom whether flashes are produced; the explosion is confined entirely to the tube and could not possibly ignite fire-damp outside. The author calculates the pressure produced by each blow to be about 30 atmospheres. The air in the tube must be changed after each trial, so as to have it filled with the air to be tested, For this purpose a loose plunger is employed, which is worked a few times up and down the tube.

The author also made experiments with Ansell's diffusion apparatus, in which the marsh-gas passes through a porous vessel and raises a caoutchouc cover which is arranged so that it may make communication with an electric bell. The action is very rapid, but the raised caoutchouc soon falls; the author devised a self-acting arrangement whereby the vessel was kept filled with nitrogen produced by the action of bleaching powder on sal-ammoniac; but this apparatus did not give indications with less than 5 per cent. of marsh-gas. W. T.

Decomposition of Gun-cotton in a Closed Vessel. By Sarrau and Vieille (*Compt. rend.*, **89**, 165—167).—The pulverulent gun-cotton used in these experiments had the composition: C, 24·0; N, 12·7; O, 55·6; H, 2·4; residue, 2·4; moisture, 2·6. Measurements of the pressures produced by deflagrating different quantities in a cylinder capable of holding 30·3 c.c., gave the following results:—

Density of products.	Pressure in kilos. per sq. cm.	Density of products.	Pressure in kilos. per sq. cm.
0·10	1,190	0·30	5,920
0·15	2,200	0·35	7,730
0·20	3,090	0·45	9,760
0·25	4,670	0·55	11,840

The heat produced by the combustion of one kilogram of the dry substance = 1,045 cals., the density of the products being 0·023 under

a pressure of 250 kilos. The volume of permanent gas measured at 0° and 760 mm. produced by 1 kilogram of the dry substance varied with the density of the products.

Density.	Volume of gas.
0·010	658·5 litres.
0·023	669·1 „
0·200	678·7 „

The composition of the gas also varied in a similar manner.

Density.	Pressure.	CO_2.	CO.	H.	N.
0·023	250	23·72	43·24	17·28	15·76
0·200	3,090	28·68	37·61	18·95	14·85
0·300	5,920	30·42	36·28	18·76	14·54

No methane, hydrocyanic acid, or nitrous vapours was formed. The amount of water produced in the experiments under the lowest pressure was equal to 15·6 per cent. of the weight of the gun-cotton employed. In all the experiments, with the exception of the determinations of the pressures, the gun-cotton was deflagrated in an atmosphere of nitrogen. When deflagrated in oxygen, the results are somewhat modified. C. H. B.

Combustion of Gunpowder. By Noble and Abel (*Compt. rend.*, **89**, 155—164).—By adopting special precautions in order to prevent oxidation by exposure to the air, the authors have been able to prove that potassium thiosulphate constitutes from 1 to 6 per cent. of the solid products of the combustion of gunpowder, a conclusion which is confirmed by comparing the amount of oxygen existing in the gunpowder with that found in the products of combustion.

The amount of thiosulphate formed depends on slight modifications in the conditions under which explosion takes place, and is not affected by differences in the proportion of gaseous and solid products. It is rapidly increased when the solid residue is exposed to the air, owing to the oxidation of the sulphide, and the temperature of the mass rises in some cases to as high as 315°. The products of combustion of blasting powder, which contains about 11 per cent. less nitre than military powders, show remarkable peculiarities.

Carbonic oxide and carbonic anhydride exist in about equal proportions, the amount of the former gas being about double that obtained from any other powder, whilst the amount of carbonic anhydride decreases from 40—45 to 32 per cent. Methane and hydrogen are present in exceptionally large proportion, and sulphuretted hydrogen is as high as 7 per cent. In the solid residue the proportion of potassium carbonate is comparatively small, and potassium sulphate is present to the extent of only 0·5 per cent. Potassium monosulphide amounts to 32 per cent., potassium thiosulphate to 6 per cent., and potassium thiocyanate to 3 per cent. Ammonium sesquicarbonate and free carbon are present in larger quantity than in any other experiments. These differences are doubtless due to the relatively small quantity of the oxidising agent existing in the powder.

Determinations of the heat produced by exploding the powders in

quantities of 9·72—12·96 grams, and 25·92 grams in cylinders capable of holding 32·5 grams and 118·8 grams respectively, gave the following numbers:—

1 gram	Waltham Abbey pebble	714·5 thermal units.
1 „	„ „ R.L.G.	718·1 „
1 „	„ „ F.G.	727·2 „
1 „	Curtis and Harvey, No. 6	755·5 „
„ „	Blasting	508·8 „
„ „	Spanish spherical	762·3 „

The heat produced depends on the composition of the powder, and on the conditions of explosion. The above numbers were obtained with powders which, as usual, contained a small quantity of water. The numbers obtained with perfectly dry powder were somewhat higher.

The following table gives the volume of permanent gas produced, calculated to 700° C. and 760 mm.

1 gram	Waltham Abbey pebble	278·3 c.c.
1 „	„ „ R.L.G.	274·2 „
1 „	„ „ F.G.	263·1 „
1 „	Curtis and Harvey, No. 6	241·0 „
1 „	Blasting.....	360·3 „
1 „	Spanish spherical.....	234·2 „

It will be seen that the volume of the gaseous products varies inversely with the amount of heat evolved: hence it would appear that the active force of different powders is not essentially different, a conclusion which has been experimentally verified for all the powders employed in these experiments. It is not possible to compare the active force of two powders by a simple calculation of the units of heat evolved on their explosion. The blasting powder used, when exploded with a gravimetric density 1, gave a tension of 44 tons on the square inch (6706 atmos.). The tension of Waltham Abbey powder exploded under similar conditions was 43 tons (6554 atmos.). The authors still regard the average temperature of explosion as 2200°, although this will vary with variations in the composition of the products of combustion. C. H. B.

Rotatory Power of Beer Worts. By J. Kjedal (*Bied. Centr.*, 1879, 57).—The author states that towards the end of the fermentation of the wort, many kinds of sugars come into question, of which the rotatory power at first lies between glucose and maltose, later on between maltose and dextrin, so that a mixture of these three substances, or more probably still, a series of carbohydrates may be present, such as those obtained by Musculus and Gruber by the action of diastase on starch (this Journal, 1878, Abstr., 778). A. J. C.

Fermentation of Must. By A. Blankenhorn and H. W. Dahlen (*Bied. Centr.*, 1879, 67—68).—Blankenhorn has stated that artificially warming the must gives a quicker fermentation and a better

wine than when the fermentation is allowed to proceed in the ordinary manner.

In this method, Dahlen shows the important fact that the maximum temperature of the fermenting liquid is not above the normal point.

This chemist has also attempted to apply practically the views of Neubauer and Moritz (*idem*, 1873, 59—60; 1874, 378—381)—that in an atmosphere of carbonic anhydride, the must ferments more quickly, —by utilising the gas evolved from the must itself.

Further experiments are needed to ensure its successful application in practice. A. J. C.

Resin-sizing of Paper. By G. Lunge (*Dingl. polyt. J.*, **231**, 459).—The theory of resin-sizing, which until recently was very much neglected by chemists, has been considerably developed by Wurster (*ibid.*, **226**, 75, 310 and 381, 227—267).

The author states that his own pupil, G. Conradin, previous to the first work of Wurster, not only discerned the true theory of resin-sizing, but also carried it out practically. It depends not as was formerly generally believed, on the precipitation of a resinate of alumina, but upon the precipitation of the free acid.

If this be so, the question might be asked, Why is it necessary to precipitate the resin-soap with sulphate of alumina? Why cannot free acid be used for this purpose? Wurster in a preliminary experiment found that free acid precipitated the resin in compact flakes, which are not fine enough for the sizing. He remarks, however, that the small quantity of free acid which frequently occurs in sulphate of alumina of commerce is wrongly feared by paper manufacturers. On the contrary, it is of use in the sizing, but he has not determined the limit beyond which the free acid will act injuriously; this is important, as it may be possible to replace a part of the sulphate of alumina with the much cheaper free acid.

This question, left open by Wurster, has been solved by Conradin. Sizing may be done just as well with free acid as with sulphate of alumina (alum cake). It is, however, not advisable to replace the sulphate of alumina entirely by free acid for the following reasons:—It is impossible to manufacture paper-pulp with an alkaline reaction into sized paper, but the acid reaction which it must have must not be produced by free acid, otherwise the free acid would act on the brass sieves, drying cylinders, and other parts of the machinery; the paper would be stained, the starch which is always used in sizing would be converted into dextrin, and the ultramarine blue used for producing better whites would be decomposed and the colour destroyed, and lastly, the free acid would act on and destroy the fibre of the paper itself.

Wurster states that an excess of sulphate of alumina is necessary to transform the resinate of alumina at first produced into basic sulphate of alumina and free resin acid.

It is necessary to add more sulphate of alumina when water is employed which contains much lime salts; and the difference in the water employed is the principal cause why different manufactories do not produce the same results, although exactly the same mixtures are em-

ployed. The author mentions the fact that of two papers examined by him, one sized entirely with sulphate of alumina and the other with a mixture of sulphuric acid and sulphate of alumina, no difference could be observed between them, and no part of the ultramarine used in improving the whiteness was in either case decomposed.

The author finds that a modification of Varrentrapp's method of introducing barium sulphate by adding to the pulp chloride of barium and then sodium sulphate, produces a much smoother and better paper by reason of the barium sulphate being better incorporated and fixed in the pulp, but instead of adding sodium sulphate, the author uses free sulphuric acid and sulphate of ammonia, and utilizes the sodium sulphate formed as a product from the decomposition of the resin soap. W. T.

Utilisation of the Residues obtained in the Manufacture of Anilin-red. (*Dingl. polyt. J.*, **232**, 96.)—It is known that the arsenic-acid process, the nitrate of mercury process, and Coupier's nitrobenzene process of preparing aniline-red give a yield of only 30 to 40 per cent. of colouring matter on the aniline originally used. The remainder forms resinous, hitherto valueless masses. It has been found that the air-dried residues give, when distilled in horizontal retorts, a distillate, which contains, besides water and ammonia, aniline, toluidine, xylidine, and their homologues, and a high boiling oil, containing, besides naphthylamine and acridine, large quantities of diphenylamine.

In Europe 750 tons of aniline-red are prepared annually. 1,500 tons of aniline oils being formed, which are at present a worthless residue. If treated by the above process, 250 tons of aniline and other bases could be recovered, of the value of 500,000 marks. D. B.

Manufacture of Methylaniline. By C. Häussermann (*Dingl. polyt. J.*, **231**, 469).—Methylaniline is generally made in Germany by heating methyl alcohol with crystallised aniline hydrochloride, whilst in France it is generally manufactured by the use of a mixture of aniline and hydrochloric acid instead of the salt.

The latter mode gives a product which yields the same amount of violet as the dimethylaniline obtained by the first-mentioned process.

The author considers the French method the better of the two, because, apart from the slight advantage in price, it is more easy to charge the autoclave with aniline and hydrochloric acid than with the aniline hydrochloride.

In place of the autoclave mentioned (*ibid.*, **230**, 245), which is of copper or thick enamelled cast-iron, he uses a 1 cm. thick enamelled vessel, which fits into a stronger outer vessel, the space between the two being filled with lead. If then the enamel becomes injured, the inner kettle can be removed for repair at less cost than sending the whole autoclave, owing to its comparatively light weight.

The mixture employed for the preparation of dimethylaniline is 100 parts of aniline, 85 parts of methyl alcohol, and 100 parts of hydrochloric acid. This mixture is heated in an oil-bath to about 230°, until the pressure reaches nearly 20 atmospheres. As soon as

the methylating process is ended the pressure falls, even when the heat is increased. W. T.

Explosive Product of a Solution of Phosphorus in Carbon Disulphide. By H. R. Procter (*Chem. News*, **39**, 245).—The author found two bottles containing this solution, which were probably five or six years old, with an orange-yellow deposit on the sides, and having read that a bottle with a similar deposit exploded violently on being broken, he threw them against a wall, and found that each exploded on breaking. The temperature of the solution was under the freezing point of water, and it is clear that some new and spontaneously combustible body had been formed. W. T.

Teak Wood. By G. Thoms (*Landw. Versuchs.-Stat.*, **23**, 413—427).—The greater portion of the results given in this paper have already appeared (this Journal, 1878, Abst., 1000). In addition to these, the author has made several complete analyses of teak wood, of which the following is the mean result:—Water, 8·46 per cent.; ash, 2·15; carbon, 47·51; hydrogen, 5·72; oxygen, 36·00; nitrogen, 0·13; total, 99·97. The percentages of carbon and hydrogen are higher than in most other woods. To this, as well as to its richness in phosphate of lime and silica, the author thinks the great hardness of the wood is due. He then proceeds to discuss at some length the problen in what form the calcium phosphate present in the wood as $CaHPO_4$ has been taken up from the soil, and comes to the conclusion that it enters the plant as soluble phosphate, $CaH_4P_2O_8$, and separates out from this. J. K. C.

Quebracho Wood. (*Dingl. polyt. J.*, **231**, 451—452).—At the Berlin Leather Exhibition, and more especially at the Paris Exhibition, quebracho wood attracted attention as a new tanning material.

Quebracho Colorado, commonly called quebracho, has a sp gr. of 1·11 to 1·13. It is very hard, and of a light or dark brownish-red colour. It contains, according to Jean (*Bull. Soc. Chem.*, **28**, 6), 15·7 per cent. of a tannin which is not identical with that in oak bark and in chestnut wood, and 2·8 per cent. of another astringent acid, which is not fixed by animal skins, and behaves with reagents like gallic acid.

Arnaudon has found it to contain a colouring matter which gives a beautiful yellow dye. The watery decoction of the wood is slightly acid.

Quebracho is as suitable as sumac for the manufacture of morocco leather, especially in the production of dark colours. W. T.

Manufacture of Artificial Mother of Pearl and of Imitations of Marble from Glue. By E. Fleck (*Dingl. polyt. J.*, **231**, 532—538).

Preservation of Meat. By F. v. Heyden and J. Eckart (*Bied. Centr.*, 1879, 63—64).

Formation of Fat from Caseïn in the Ripening of Cheese. By G. Murso and A. Menozzi (*Bied. Centr.*, 1879, 62—63).

General and Physical Chemistry.

Presence in the Solar Spectrum of Dark Lines, which correspond closely with the Lines of the Spectrum of Oxygen. By J. C. Draper (*Am. J. Sci.*, **16**, 256—265).—The author commences with a detailed description of his apparatus and mode of working. The photographs which he obtained were carefully compared with the maps of Ångström and others, and with the spectrum of pure oxygen. It was seen that a large number of lines in Ångström's maps, unassigned to other elements, and also a number of new lines, not given by Ångström, corresponded accurately, or very closely, with the lines in the electric spectrum of pure oxygen. A table is given including the lines from wave-length 3864·50 to 4704·65, in which forty-one lines are given as probable oxygen lines; there are but few lines beyond the above limits.

All these lines are extremely faint, showing that oxygen has but a feeble absorptive power when compared with metallic gases like hydrogen, iron, or calcium. C. W. W.

Distillation of Liquids under the Influence of Static Electricity. By D. Gerney (*Compt. rend.*, **89**, 303—305 and 348—350).—The apparatus used in these experiments resembles an inverted **U**-tube. A platinum wire passes through each of the closed extremities of the limbs of the tube. The liquid to be experimented on is brought into each limb of the apparatus through a lateral opening. The air is then exhausted by means of an air-pump, and the apparatus is sealed at the blowpipe.

On connecting the platinum wires with the poles of a Holtz's electrical machine, the liquid passes from the limb attached to the positive pole to that connected with the negative. That the distillation is not due to the difference in temperature between the two poles, is shown by an ingenious modification of the apparatus, in which the vessel in connection with the positive pole is surrounded by the liquid connected with the negative pole or *vice versâ*, when the distillation proceeds as usual.

Moreover, the liquid will pass from the positive to the negative pole, even if the temperature of the latter is 20° higher than that of the former.

The quantity of liquid transferred from one tube to the other is proportional to the amount of electricity employed, and does not depend on the area of the surface of the liquid.

When the electric current is passed through the liquid contained in the apparatus above described, the liquid gradually ascends the sides of the tubes. If the interior of the apparatus is covered with a coating of paraffin, or any other substance which prevents the liquid wetting the tubes, then the distillation will no longer take place. The increase in bulk of the liquid in contact with the negative pole is not produced by the condensation of vapour arising from the evapora-

tion of the positive liquid, but is entirely due to the flow of liquid up the sides of the positive tube down to the negative. The liquid is capable of being transported when the surfaces of the negative and positive fluids are 0·6 meter apart.

No relation could be ascertained between the rate of transportation of different liquids and their constants of capillarity. The rate of transporation is larger for feeble than for good conductors of electricity, *e.g.*, the addition of a minute quantity of an acid or an alkali to water reduces its transportability to $\frac{1}{50}$. W. C. W.

The Electromotive Force produced by the Flow of Liquids through Tubes. By E. Edlund (*Ann. Phys. Chem.* [2], **8**, 119—137).—This is merely a reply to an attack by Dorn (*Ann. Phys. Chem.*, 1878, 20) on two previous communications of the author (*ibid.*, 1877, 161; and 1878, 489), who now, by further experiments, fully confirms his previous results. T. C.

The Electromotive Power of a Grove's Element in Terms of Siemens-Weber Units. By E. Riecke (*Ann. Phys. Chem.* [2], **8**, 183—184).—This paper is essentially a correction of a former determination (*Ann. Phys. Chem.*, 1878, 36), of the electromotive power of a Grove's element, as determined by Ohm's method. The author now finds that the electromotive power of such an element is equal to 19·48, expressed in Siemens-Weber units. Kohlrausch, Crova, and Fromme found for this value the numbers 19·09, 19·89, and 19·62 respectively. T. C.

The Electromotive Power of Gas Elements. By B. Osgood Pierce (*Ann. Phys. Chem.* [2], **8**, 98—119).—The following results were obtained at the ordinary temperature:—

Combinations.	Liquid.	Electromotive power. D = 1.	Combinations.	Liquid.	Electromotive power. D = 1.
H and O	Water	0·874	I and Br	Water	0·335
H ,, N_2O	,,	0·790	H ,, Br	NaBr + Aq.	1·252
H ,, CO_2	,,	0·981	H ,, Br	KBr + Aq.	1·253
H ,, NO	,,	0·933	O ,, Br	,,	0·500
H ,, air	,,	0·807	O ,, I	KI + Aq.	0·057
H ,, H_2O	,,	0·807	H ,, I	,,	0·861
H ,, CO	,,	0·404	H ,, NO	HCl + Aq.	0·765
H ,, O	H_2SO_4 + Aq.	0·926	H ,, O	,,	0·855
H ,, CO_2	,,	0·892	H ,, Cl	,,	1·360
H ,, NO	,,	0·768	H ,, Cl	KCl + Aq.	1·390
H ,, O	Na_2SO_4 + Aq.	0·698	H ,, Cl	NaCl + Aq.	1·390
H ,, O	K_2SO_4 + Aq.	0·698	H ,, O	,,	0·766
H ,, O	$ZnSO_4$ + Aq.	0·771	H ,, CO_2	,,	0·846
H ,, CO_2	,,	0·820	H ,, NO	,,	0·750
H ,, NO	,,	0·860			

At a temperature of 75—80° the following results were obtained:—

Combinations.	Liquid.	Electromotive power. D = 1.	Combinations.	Liquid.	Electromotive power. D = 1.
H and O	Water	0·828	H and N_2O	Water	0·780
H „ NO	„	0·945	H „ H_2O	„	0·954
H „ CO_2	„	0·875			

The above table shows that the nature of the liquid has great influence on the electromotive power of any combination of two gases.

T. C.

The Thermoelectric Position and Electric Conductivity of Steel in their Relation to its Hardness. By C. Barus (*Ann. Phys. Chem.* [2], **7**, 383—414).—Previous researches of Ruths (*Inaug. Dissertation*, p. 34, Darmstadt, 1874), Rowland (*Phil. Mag.* [4], **50**, 361), Gaugain (*Compt. rend.*, **82**, 145), Fromme (*Gött. Nachr.*, **157**, 1876), Trève and Durassier (*Ann. Chim. Phys.* [5], **5**, 266), and Gray (*Phil. Mag.* [5], **6**, 321), have shown that the condition of hardness of a steel rod exercises a great but complicated influence on its magnetic properties. In the present communication, the author endeavours to show that the thermoelectric position and resistance of a steel bar may be employed as a measure of its degree of hardness. If a thermo-element, constructed of a steel rod hardened by quenching, and a soft bar, be heated, a current is produced, which at the heated side passes from the hard to the soft metal, and whose electromotive power, with one and the same element, is proportional to the difference of temperature of the points of soldering. With different elements, the electromotive power increases with the difference of temperature, and also with the difference in hardness of the two steel bars. The limiting value of the ratio of the electromotive power of a thermo-element (consisting of an annealed and any hard steel bar) to the difference of temperature (if the latter converges towards zero, and the colder point of soldering be maintained at 0°) is taken as a measure of the hardness of a tempered rod, and is termed the *thermo-electric hardness* (T. E. H.). The following are the more important results obtained:—(1.) With steel rods made of the same kind of wire, the thermoelectric position always varies with the mechanical hardness. (2.) For annealed and for equally tempered bars, the thermoelectric hardness (T. E. H.) of rods, hardened under similar conditions, has nearly the same value. (3.) The T. E. H. of rods hardened by sudden cooling, varies considerably, according to their thickness. (4.) The T. E. H. does not increase regularly with the temperature of the rod at the time of quenching, but at a temperature corresponding with the commencement of a dark-red heat, it becomes suddenly brittle; from this temperature onwards, however, the increase in hardness varies constantly with the temperature. Since the specific gravity of steel increases with its hardness if the latter be produced by wire-drawing, but diminishes if it be produced by quenching, and since the heat-current in a thermo-element passes from the soft to the hard-drawn wire, that is, in a direction the

reverse of that in the case of wires hardened by quenching; and since also the specific resistance of steel is diminished by drawing, but increased by quenching, we must distinguish between a purely mechanical and a chemical hardness, the latter being due chiefly to the chemical combination with carbon. In consequence of the mechanical phenomena accompanying quenching, the degree of chemical hardness is modified by the dimensions and form of the rod. (5.) The T. E. H. can, therefore, only be considered as a measure of the degree of hardness if the rod under investigation has a uniform degree of hardness throughout its entire mass, and this is approximately the case if thin rods be hardened by the method described in the original paper. (6.) If the hardness of steel produced by quenching be due to the combination of carbon, soft iron and annealed steel should stand very near to one another thermoelectrically, and this is in fact the case. The minimum values of the T. E. H., which are obtained by annealing, are nearly equal for different steels and bar irons, whereas the maximum values (obtained by quenching) vary considerably with the composition of the steel, increasing with the percentage of carbon. (7.) The results obtained by Fromme (*loc. cit.*) with regard to the influence of hardness on the specific gravity of steel agree with those of the author, as deduced from the T. E. H. (8.) The specific resistance of steel increases with the hardness, and the maximum value of specific resistance, which can be imparted to a steel rod by hardening, depends on the thickness of the rod. The increase in the specific resistance is approximately proportional to the thermoelectric hardness. The specific resistance of a steel bar can be increased almost threefold by hardening, and as a general rule the thermo-current passes from the bar with the greater to that with the less resistance. The specific resistance of annealed steel, like the T. E. H., is nearly equal to that of annealed iron.

Steel bars are divisible into two classes, one of which (the harder) is electronegative in respect to copper, and the other (the softer) electropositive. With the former, the T. E. H. is greater than 107·10°, and with the latter less. By the following means, the hardness of a mass of steel of any form may be easily determined in reference to a number of standard bars of known hardness:—A steel bar of known hardness is broken into two parts, and one end of each half is connected with a galvanometer, the block of steel (of any form) to be tested is then placed in contact with the other ends (T and *t* respectively), and the place of contact T is heated. If the mass of steel in the neighbourhood of the end T is softer than the standard bar, then the thermo-current will pass from the latter to the former, but in a reverse direction in the other case. A similar method may be used to ascertain the state of homogeneity of a mass of steel or iron, for it is only necessary to use a small bar of the same as the test-bar to the remainder.

It is also proposed to apply the above facts to the determination of the magnetic moment of permanent magnetism. T. C.

Magnetic Behaviour of Finely-divided Iron. By A. v. Waltenhofen (*Ann. Phys. Chem.* [2], **7**, 415—426).—The magnetic

induction of finely-divided iron, even with the strongest currents employed, is one-fifth smaller than that of massive iron of equal weight and under similar circumstances, and is still less in the case of weak currents. This can be ascribed only to the circumstance that the finely-divided iron consists of a number of particles, the distances between which are very great compared with those in the case of bar iron; and, consequently, the reciprocal influence of the particles, which increases the action of the magnetic current, becomes infinitely small. This influence diminishes with the third power of the distance.

From the fact that the specific magnetisation of finely-divided iron is only one-fifth of that of bar iron, it follows *that the magnetic moment which an iron bar assumes in a magnetising spiral, depends in great part on the reciprocal magnetic action of its molecules*, the direct rotation of which by the current is only a small fraction of the induced magnetism.

That the different behaviour of finely-divided and massive iron is due to their reciprocal magnetic influence, which is in turn dependent on the greater or lesser disintegration of the molecules, is confirmed by the fact that the specific magnetisation depends also on the density of the finely-divided iron, for it is greater when the iron powder is tightly packed than when it is but loosely aggregated. T. C.

Conductivity of Liquids for Heat. By W. Beetz (*Ann. Phys. Chem.* [2], **7**, 435—460).—Previous researches on this subject have given results which are by no means concordant, for one and the same liquid appears, according to one investigator, as a better conductor, and, according to another, as a worse conductor of heat than water. The following represent the order of conducting powers for heat of various liquids as determined by the author:—

Between 8° *and* 14°: Mercury 1066, carbon bisulphide 513, chloroform 468, ether 465, water 413, benzene 409, sulphuric acid 376, alcohol 360, glycerol 340, olive oil 266.

Between 36° *and* 28°: Mercury 1310, carbon bisulphide 738, water 662, chloroform 648, benzene 593, alcohol 570, sulphuric acid 451, glycerol 386, olive oil 308.

These results agree with those obtained by Winkelmann, but are very different from those of Guthrie, according to whom chloroform was a worse conductor than any other liquid submitted to experiment. The method employed by Guthrie is not applicable to liquids which do not wet glass, and hence mercury cannot be strictly compared with the other liquids. The above lists show that the relative conducting powers vary with the temperature. The conducting power of a given liquid, as previously pointed out by Guthrie, increases with the temperature. As a general rule, to which, however, alcohol is a marked exception, the most easily volatile liquids are likewise the best conductors. No effect appears to be produced by colouring the liquids with various dyes. Tables are also given showing the conductivity of various saline solutions, from which it seems that at lower temperatures water gains in conducting power by dissolving in it different salts, and this is especially the case with dilute solutions. At higher temperatures

water is a better conductor than all aqueous solutions, except those of sodium chloride and cupric chloride. Most salts have a maximum of conductivity at a certain degree of concentration. The conductivity of a mixture of two liquids is the mean of those of the several liquids.

By diminishing the mobility of water by mixing with it various thickenings as starch-paste and emulsion of quince-juice, it is shown that the phenomena of the heat-conductivity of liquids depend, like their electric conductivity (Kohlrausch, *Wied. Ann.*, **6**, 1) on the molecular friction. T. C.

The Specific Heat of Water. By S. Henrichsen (*Ann. Phys. Chem.* [2], **8**, 83—92).—As the result of a large number of experiments with Bunsen's ice-calorimeter, the specific heat of water at any temperature, t° is given by the following equation:—

$C_t = 1 + 0{\cdot}0003156t + 0{\cdot}000004045t^2$.
$C_t = 1 + 0{\cdot}00004t + 0{\cdot}0000009t^2$ (Regnault).
$C_t = 1 + 0{\cdot}00110t + 0{\cdot}0000012t^2$ (Jamin and Amaury).
$C_t = 1 + 0{\cdot}00030192t$ (Münchhausen).

Calculated by the above, the specific heat of water at 100° is as follows:—

Regnault.	Jamin and Amaury.	Stamo.	Münchhausen.	Henrichsen.
1·013	1·122	1·125	1·030	1·071

The author's experiments, therefore, give a result which is nearly the mean of those of Regnault and Jamin. T. C.

Expansion of Solid and Liquid Bodies. By H. F. Wiebe (*Chem. News*, **40**, 154).—The following conclusions have been arrived at:—

(1.) The product of an atomic volume and the cubical expansion-coefficient represents *the absolute expansion of an atom. The absolute expansion of atoms is a periodical function of the atomic weight.*

(2.) Expansion of a body represents that part of heat necessary to supersede its cohesive power. Suppose the density of a body to be d, its atomic weight a, its cubical expansion-coefficient α, its specific heat c, its boiling point s, and its melting point σ, we have the following relation:—

$$\frac{\frac{d}{\alpha.a}}{d.c(s-\sigma)} = 2; \text{ or } 2\ \alpha.a.c(s-\sigma) = 1.$$

(3.) In gaseous substances, the molecules are so far separated as no longer to influence one another. Liquid and solid bodies consist of molecular groups, which evidently are formed by those especial powers, emanating from the molecules themselves. At the boiling point as well as at that of melting, *all bodies have an equal degree of cohesion.* Therefore, by multiplying the absolute expansion of an atom

into the temperatures of these fixed points (the temperatures having been previously augmented by the inverted expansion-coefficient), the result will be comparable figure-values, *all of which are multiples of the expansion-coefficient.*

In the following table in the column immediately following the elements, the figures representing the absolute expansion of the atom are given; the second and third columns contain respectively the melting point on the common scale and in so-called absolute temperature; the fourth shows the product of the absolute expansion and temperature; and the fifth the expansion-coefficient and a constant—characteristic of each matter—expressed by the letter m:—

	I.	II.	III.	IV.	V.	*m.*
S.....	0·003015	113·6	388·6	1·171629	0·003905	300
Se	0·001872	217	492	0·921024	0·003607	250
Te	0·001029	489	764	0·786156	0·003931	200
Zn	0·000795	412	687	0·546165	0·003641	150
Cd	0·001188	315	590	0·700920	0·003505	200
As	0·000222	500	775	0·172050	0·003721	50
Sb	0·000630	430	705	0·444150	0·003701	120
Bi	0·000864	264	539	0·465696	0·003725	125
In	0·001911	176	451	0·861861	0·003591	240
Tl	0·001557	290	565	0·879705	0·003665	240
Pl	0·001530	334	609	0·931770	0·003728	250
Fe	0·000255	1600	1875	0·478125	0·003678	130
Co	0·000255	1500	1775	0·452625	0·003621	125
Ni	0·000255	1450	1725	0·439875	0·003665	120

Without at present enlarging on these constants as to their explanation, it is simply wished to point out the fact that they seem to be *in relation with the number of atoms, combining to form a solid molecular group; constants show, for elements of the same chemical group, simple proportions.* To the boiling point similar proportions are applicable; the following relation is therefore generally adopted:— $\frac{a.\alpha}{d}.\ T = \beta.\ m$, in which β represents the expansion-coefficient; T the difference of temperature between the boiling and the melting point, or from the latter to the absolute zero point; and α the medium expansion-coefficient within these limits of temperature.

It appears that the "Gay-Lussac rule" is generally valid, quantitatively changed only in its application to the fluid and solid state of matter: hence a common law of expansion is applicable to the whole scale of the state of aggregation in matter.

(4.) Applying the equation $\frac{a.\alpha}{d}.\ T = \beta.\ m$ to homologous series of organic bodies, proportions astonishingly simple are the results. It is shown that *for the acids, the constant* 5·2 *is to be multiplied by the number of atoms of hydrogen contained in the gaseous molecule* + 1; *for the series of alcohols, the constant* 8·5 *by half the number of atoms of hydrogen.*

This subject is very soon to be treated more fully, especially in reference to the theoretical significance of the constant m. D. B.

Compressibility of Gases at High Pressures. By E. H. Amagat (*Compt. rend.*, **89**, 437).—In a previous paper the author has given the results obtained with nitrogen between the pressures of 127 and 430 atmospheres. He now gives the results for a number of other gases between 30 and 430 atmospheres. All the gases studied, except hydrogen, showed a minimum of the value pv, situated at the following pressures, expressed in meters of mercury:—Nitrogen, 50; oxygen, 100; air, 65; carbonic oxide, 50; methane, 120; ethylene, 65.

It is thus seen that the gases which are nearest to the conditions which determine their liquefaction are those which attain the greatest compressibility. Ethylene in particular exhibits extraordinary variations of compressibility, the quotient $\frac{pv}{p'v'}$ varying between 2·213 and 0·337. It seems probable that when a gas submitted to increasing pressure shows a decrease in compressibility (after first possibly showing an increase), it is under such conditions that, according to Andrews, it can be made, by pressure alone, to pass through all the intermediate stages between the gaseous state and the liquid state, without being actually liquefied: a diminution of compressibility therefore generally indicates that a gas is at a temperature higher than its critical point.

Nitrogen, oxygen, air, hydrogen, carbonic oxide, and methane are in this class, and ethylene also, at the temperatures at which these experiments were made. The great variations of compressibility shown by this gas indicate that it is near its critical point; the variations would doubtless disappear at higher temperatures. C. W. W.

Some Specific Gravity Determinations. By F. W. Clarke (*Amer. J. Sci.* [3], **16**, 201).—The following specific gravity determinations (p. 1005) are referred to water at 4° as unity; they were all taken in benzene.

Thallium tellurate.—Metallic thallium is not attacked by telluric acid, even at the boiling heat. When a solution of ammonium tellurate is added to one of thallium nitrate, a heavy white precipitate falls, which, when dried at 100°, has a specific gravity of 5·687 at 22° and 5·712 at 20°. Heated to 180° it loses 1·46 per cent. of water, and turns a pale straw colour. The sp. gr. of this salt is 6·742 at 16° and 6·760 at 17·5°. At a red heat the thallium tellurate fuses and is reduced to tellurite, which forms a clear yellow glass when cold.

Formula.	Sp. gr. at $t°$.	Formula.	Sp. gr. at $t°$.
$HgCy_2$*	4·0262 at 12°	$CdCl_2.BaCl_2.4H_2O$	2·996 at 25·2°
„	4·0036 „ 14·2	$KMeCOS_2$	1·7002 „ 15·2
„	4·0026 „ 22·2	„	1·6754 „ 15·2
$HgCy_2.HgO$	4·437 „ 19·2	$KEtCOS_2$	1·5564 „ 18·2
„	4·428 „ 23·2	„	1·5576 „ 21·5
„	4·419 „ 23·2	„	1·5580 „ 21
$HgCy_2.HgCl_2$	4·531 „ 21·7	$K(C_4H_9)\beta COS_2$	1·3713 „ 15
„	4·514 „ 26	„	1·3832 „ 14·5
$2KCy.HgCy_2$	2·447 „ 21·2	$Co(CHO_2)_2.2H_2O$	2·1286 „ 22
„	2·462 „ 21·5	$Ni(CHO_2)_2.2H_2O$	2·1547 „ 20·2
„	2·455 „ 24	$Co(C_2H_3O_2)_2.4H_2O$	1·7031 „ 15·7
$HgBr_2$†	5·7461 „ 18	„	1·7043 „ 18·7
„	5·7298 „ 16	$Ni(C_2H_3O_2)_2.4H_2O$	1·7443 „ 15·7
$HgBr_2.KBr$	4·412 „ 17·2	„	1·7346 „ 17·2
„	4·419 „ 24·5	$BaMe_2(SO_4)_2.2H_2O$	2·273 „ 19·2
„	4·3996 „ 20·5	„	2·279 „ 21·2
$HgBr_2.KBr.H_2O$	3·867 „ 20–24	$BaEt_2(SO_4)_2$	2·080 „ 21·7
KBr‡	2·712 „ 12·7	„	2·0714 „ 22·6
$(NH_4)_2Cr_2O_7.HgCl_2.H_2O$	3·329 „ 21	$BaPr_2a(SO_4)_2$	1·839 „ 20·5
HgI_2§	6·231 „ 10–19	„	1·844 „ 20·5
$2(KI.HgI_2).3H_2O$	4·289 „ 23·5	$Ba(C_5H_{11})_2(SO_4)_2$	1·623 „ 21·2
„	4·254 „ 22	„	1·632 „ 22
$NMe_4I.HgI_2$	4·003 „ 23·2	$PtCl_2.2KCl$	3·2909 „ 21
„	3·976 „ 23·5	„	3·3056 „ 20·3
„	3·968 „ 24	$H_2TeO_4.2H_2O$	2 9999 „ 25·5
„	3·971 „ 24	„	2·9649 „ 26·5
$CdCl_2$‖	3·938 „ 23	H_2TeO_4	3·425 „ 18·8
$CdCl_2.2H_2O$	3·339 „ 18·2	„	3·458 „ 19·1
„	3·320 „ 23·2	„	3·440 „ 19·2
„	3·314 „ 23·6	$(NH_4)TeO_4$	3·024 „ 24·5
$2CdCl_2.SrCl_2.7H_2O$	2·718 „ 24	„	3·012 „ 25
$CdCl_2.BaCl_2.4H_2O$	2·952 „ 24·5		

C. W. W.

Changes in the Surface of Platinum and Palladium produced by Oxygen-Polarisation. By K. R. Koch (*Ann. Phys. Chem.* [2], **8**, 92—97).—The irregularity in the amount of friction proved by Warburg and Babo (*Ann. Phys. Chem.*, 1877, 406) to occur between two rubbing surfaces in the presence of a liquid, disappears according to Lippman (*Pogg. Ann.*, **149**, 550) in the case of mercury and dilute sulphuric acid, if the electromotive force on the rubbing surfaces is kept constant. The author has investigated the influence of polarisation on the friction between two surfaces separated by a liquid stratum, and finds that (in the case of platinum or palladium separated from a surface of glass by water or dilute sulphuric acid) the friction considerably increases when the rubbing surface was the anode, but did not change when it was the cathode. Hydrogen-

* 3·77 at 13°, Bödeker (*Jahresb.*, 1860).
† 5·9202, Karsten (*Schweigg. Jour.*, **5**, 65).
‡ 2·69, Schröder (*Pogg. Ann.*, 1859).
§ 6·25 Filhol (*Ann. Chim. Phys.* [3], **21**, 1847.
‖ 3·6254 at 12°, Bödeker (*Jahresb.*, 1860).

polarisation does not affect the friction, whilst oxygen-polarisation considerably increases it; this increase immediately disappears on reversing the current, but only gradually on interrupting it. These phenomena are probably of a mechanical nature only, and are not due to the electrolytic oxygen attacking the metal. In the case of gold, the friction is not affected by oxygen-polarisation. T. C.

Employment of Diffusion in the Study of the Phenomena of Dissociation. By L. Troost (*Compt. rend.*, **89**, 306—308).—Deville pointed out twenty-five years ago (*Ann. Chim. Phys.* [3], **58**, 275) that it is impossible to decide by means of diffusion whether a given body is capable of existing in the gaseous state without dissociation taking place. Free hydrogen and oxygen can be obtained from steam at 1000° by diffusion, although at this temperature the tension of dissociation of steam is so small that the density of the vapour is not perceptibly diminished by the presence of the free elements.

The recent experiments of Naumann (*Ber.*, **12**, 738, and 1879) on the dissociation of chloral hydrate, have therefore no bearing on the question of the existence or non-existence of this compound in the gaseous state. W. C. W.

Remarks on a Note on Chloral Hydrate by Wurtz. By Berthelot (*Compt. rend.*, **89**, 271—273).—The author considers that the errors of experiment attending the use of the apparatus employed by Wurtz would render imperceptible the small amount of heat which would be liberated when steam and chloral vapour are brought together.

In a reply to Berthelot's remarks on the author's note on chloral hydrate, Wurtz (*Compt. rend.*, **89**, 337—338) denies that his apparatus is not sufficiently sensitive to indicate an increase in temperature, when steam and chloral vapour are brought together, in case combination between these two bodies takes place. W. C. W.

Researches on the Decomposition of Metallic Salts, and on certain Inverse Reactions which take place in Presence of Water. By A. Ditte (*Ann. Chim. Phys.* [5], **14**, 190—238).—According to Berthollet's laws an acid decomposes a salt (1) when an insoluble acid or one less soluble than the reacting acid can be produced by the decomposition, (2) when a more volatile acid can be produced, and (3) when an insoluble salt or one less soluble can be formed. These laws are generally correct, but in many cases other reactions take place, *e.g.*, the production of lead chloride by the action of hydrochloric acid on lead sulphate, and it is these and similar reactions which are studied in the present paper.

Lead Sulphate and Hydrochloric Acid; Lead Chloride and Sulphuric Acid.—A solution of hydrochloric acid of known strength is placed in contact with excess of lead sulphate, and after 24 hours' action at a constant temperature, the free sulphuric acid is estimated in the liquid, and the free hydrochloric acid calculated from it. Ignoring the trace of lead found in hydrochloric acid, and the solubility of lead

sulphate in the liquid, the quantity of lead sulphate decomposed is thereby ascertained. From the table of observations given, it is seen that at temperatures about 16°, solutions of hydrochloric acid attack lead sulphate as soon as they contain more than 7 grams of HCl per litre, and the quantity of salt decomposed is greater as the acid is stronger.

The reaction is always complete after 24 hours, after which the materials exercise no action on one another, the sulphuric acid not decomposing the dissolved lead chloride, and the hydrochloric acid not attacking the remaining lead sulphate.

If now a solution in this state is heated to a certain temperature, and maintained at that temperature for some time, and the quantities of lead, sulphuric acid, and hydrochloric acid are estimated in the liquid, it is found that as the temperature rises a larger quantity of lead sulphate is decomposed, the free sulphuric acid increasing, and the free hydrochloric acid diminishing in the liquid.

The following table shows this reaction for a liquid containing 37·34 grams of HCl per litre :—

	Initial liquid.	Final liquid.	
Temperature.	HCl.	HCl.	SO_3.
16°	37·34	33·80	3·87
42	,,	33·12	4·63
50	,,	32·85	4·90
70	,,	32·43	5·38
100	,,	30·46	7·54

The quantity of lead sulphate remaining in excess exercises no influence on the results. For the inverse reaction, that of sulphuric acid on lead chloride, the results are as follows. A solution of sulphuric acid in contact with excess of lead chloride decomposes a quantity of that salt, which is larger as the strength of the acid is greater, but on raising the temperature the quantity of free sulphuric acid increases, lead chloride being reproduced. This result is shown in the following table, an abstract of a larger one :—

	Initial liquid.	Final liquid.	
Temperature.	SO_3.	SO_3.	HCl.
16°	76·97	20·03	51·93
50	,,	22·77	49·42
70	,,	26·78	45·86

The quantities are in grams per litre of the anhydrous acids.

A solution of sulphuric acid containing less than 7·67 grams of SO_3 per litre (= 7 grams HCl) loses all its free sulphuric acid in contact with excess of lead chloride, free hydrochloric acid and lead chloride being alone present in the liquid.

If a solution of hydrochloric acid of a certain strength, with excess of lead sulphate, and a solution of sulphuric acid of exactly equivalent strength, with excess of lead chloride, be maintained at the

same temperature until both have attained a state of equilibrium, they will be found to have the same composition in free acids.

Let us consider a solution which is in equilibrium at t degrees, containing the quantities a and b of free hydrochloric and sulphuric acids, and suppose the temperature raised to t' degrees; the materials present will react on one another till a new state of equilibrium is attained, the liquid now containing the quantities a' b' of free acids. If the liquid be allowed to cool again to the original temperature, t, the chloride of lead which was simply dissolved crystallises out, but the liquid never returns to its original composition at t. A reaction inverse to that set up on heating certainly takes place on cooling, but it soon ceases, and the quantities of free acid present hold each other in equilibrium. In fact there exists at any given temperature an infinite number of values of a and b capable of equilibrating each other; by heating the liquid, or by adding more acid, the conditions are changed, and the values of a and b correspond to a liquid of different composition.

The quantities of free acid capable of equilibrating each other in a liquid of known composition at a given temperature, in contact with excess of lead salt, may be found by the following equations:—

Suppose a liquid containing A per cent. of hydrochloric acid, and at t degrees. Let y be the quantity of free sulphuric acid, and x the quantity of free hydrochloric acid in the liquid after equilibrium is attained; then (1) $x = \mathrm{A} - y\,\frac{36{\cdot}5}{40} = \mathrm{A} - 0{\cdot}912\,y$.

Suppose, on the other hand, a solution containing B per cent. of sulphuric acid at t, and let x be the weight of free HCl, and y that of the SO_3 remaining; then $y = \mathrm{B} - x\,\frac{40}{36{\cdot}5} = \mathrm{B} - 1{\cdot}096\,x$. If the liquids contained equivalent quantities of the two acids, then $\mathrm{B} = 1{\cdot}096\,\mathrm{A}$; whence $y = 1{\cdot}096\ (\mathrm{A} - x)$, or $\frac{y}{1{\cdot}096} = 0{\cdot}912\,y = \mathrm{A} - x$, or $x = \mathrm{A} - 0{\cdot}912\,y$, which is equation (1).

Hydrobromic acid decomposes lead sulphate just as hydrochloric acid does, in larger proportion as it is more concentrated, the quantities of free acid equilibrating one another after some time. On heating the liquid, however, the quantity of lead sulphate decomposed diminishes, instead of increasing as with hydrochloric acid. Moreover, in somewhat concentrated liquids, the hydrobromic acid is decomposed above 50°, so that exact determinations are not possible. On cooling, the liquid—in this respect resembling hydrochloric acid—does not return to its original composition, there being an infinite number of quantities of free acid capable of equilibrating one another, the raising of the temperature being equivalent to the addition of free acid. Here, as with hydrochloric acid, we may construct curves which will give the final composition of a liquid containing a known quantity of free acid placed in contact with excess of the corresponding lead salt at a given temperature.

Hydriodic acid resembles hydrobromic acid in its action on lead sulphate, the quantity of free sulphuric acid diminishing as a cold solution

which has attained equilibrium is heated. The two sets of curves representing this action are nearly straight lines; they bend very slightly towards the horizontal axis and in the direction contrary to that of the curves of hydrochloric and hydrobromic acids; at the same time they rise rapidly and approach a position parallel to the axis of sulphuric acid, more and more as they correspond to a higher temperature.

Hydrofluoric acid has no action on lead sulphate.

Lead Sulphate and Sodium Chloride; Lead Chloride and Sodium Sulphate.—Sulphate of lead dissolves in a solution of sodium chloride with slight evolution of heat; on cooling, lead chloride crystallises out. Sodium sulphate and lead chloride produce lead sulphate and sodium chloride. The action of sodium chloride on lead sulphate is much less energetic than that of hydrochloric acid, and the changes produced by heat resemble those which take place with hydrobromic and hydriodic acids, *i.e.*, the quantity of free sulphuric acid in the liquid diminishes, lead sulphate being reproduced. This property of sodium chloride and other chlorides renders it impossible to estimate lead as sulphate in presence of chlorides.

Lead Sulphate and Potassium Chloride; Lead Chloride and Potassium Sulphate.—The action of potassium chloride on lead sulphate is modified by the production of a double sulphate of lead and potassium, and by the action of water alone and of solutions of lead chloride on this double sulphate.* If to a liquid containing 300 grams per litre of potassium chloride we add a small quantity (4·13 grams per litre) of lead sulphate, it immediately dissolves, and after some time the liquid deposits the greater portion of the lead as chloride.

If now we add a second equal quantity of lead sulphate, it no longer dissolves, but is slowly converted into chloride, the potassium sulphate thereby formed again dissolving in the liquid. If a third quantity of lead sulphate be now added, it combines with the potassium sulphate to form the double salt $PbSO_4.K_2SO_4$. This salt is decomposed by water, a small quantity of potassium sulphate going into solution. Its decomposition may be entirely prevented by previously dissolving a small quantity of that salt in the water. The presence in the water of salts having no action on the sulphate of potassium exercises no influence on the decomposition of the double salt, but if the water contains chloride of lead, the quantity of potassium sulphate taken up by the water is greatly diminished.

The same phenomena are observed in the action of potassium sulphate on lead chloride.

Lead Sulphate and Ammonium Chloride; Lead Chloride and Ammonium Sulphate.—Precisely similar action to that in the case of the corresponding potassium salts, a double sulphate of lead and ammonium, $PbSO_4.(NH_2)_2SO_4$, being formed, and this salt being decomposed by water and solution of lead chloride just as in the case of the lead-potassium sulphate. A concentrated solution of ammonium chloride placed in contact with excess of lead sulphate changes quickly into a thick mass of crystals of the above double sulphate.

* Recherches sur la décomposition des sels metalliques par l'eau (*Annales de l'École Normale Supérieure*, [2], **4**, March, 1876).

The action of *potassium bromide* on lead sulphate is precisely the same as that of potassium chloride.

Zinc Sulphate and Lead Bromide; Zinc Bromide and Lead Sulphate.—A solution of zinc sulphate in contact with excess of lead bromide gives bromide of zinc and sulphate of lead. At higher temperatures the amount of action is less than in the cold. The same effect is seen in the action of zinc bromide on lead sulphate. This reaction affords a convenient method for the preparation of zinc bromide.

The reaction of *potassium iodide* with *lead sulphate* resembles the corresponding reaction with the chloride and bromide. The first portions of lead sulphate are converted into iodide, the potassium sulphate thereby formed accumulating in the liquid up to a certain point depending on the temperature, and after that combining with the excess of lead sulphate to form the double salt mentioned before.

Magnesium sulphate attacks *lead iodide* just as zinc sulphate attacks the bromide, the reactions being strictly comparable. The reaction of lead sulphate with *potassium fluoride* differs from the reactions with the other haloïd salts, on account of the very slight solubility of lead fluoride. When we add sulphate of lead to potassium fluoride, the potassium sulphate at first increases to a maximum; the double sulphate is then formed, and equilibrium is established, which is the same for all temperatures.

Potassium Cyanide and Lead Sulphate.—The same result as with potassium fluoride, lead cyanide being, however, slightly more soluble than the fluoride.

Lead Sulphate and Alkaline Carbonates.—When excess of lead sulphate is added to a solution of *potassium carbonate*, the latter disappears entirely from the solution. If twice the theoretical quantity of lead sulphate were added, it would be expected that the potassium sulphate formed would combine with the excess of lead sulphate to form the double sulphate; but this takes place up to a certain point only, for the lead carbonate formed in the reaction combines with the excess of lead sulphate present to form a body having the composition of leadhillite, $PbSO_4.3PbCO_3$.

Sodium carbonate decomposes lead sulphate entirely, forming sodium sulphate and lead carbonate. No double salt of sodium and lead sulphate is formed.

Normal carbonate of ammonia gives a reaction precisely similar to that of potassium carbonate.

An aqueous solution of carbonic acid at the ordinary pressure has no action on lead sulphate.

Potassium chlorate decomposes lead sulphate, with formation of lead chlorate and the double sulphate of lead and potassium.

When strong aqueous *ammonia* is added to lead sulphate, a brisk reaction takes place, and the mixture solidifies, all smell of ammonia disappearing if sufficient lead sulphate be present. With more dilute solutions it is observed that the action of the ammonia is to form ammonium sulphate and lead oxide, the latter then combining with excess of lead sulphate to form a basic sulphate, $SO_3.2PbO$. If sufficient lead sulphate be present, the double lead-ammonium sulphate is also formed.

Nitric acid does not decompose sulphate of lead, but dissolves a quantity which varies with the strength of the acid and with the temperature.

With an acid containing less than 445 grams N_2O_5 per litre, the quantity of lead sulphate dissolved increases with the temperature, but with stronger solutions, the action of heat is reversed, the quantity of lead sulphate dissolved decreasing with the rise of temperature. With fuming nitric acid (800 grams per litre) at 50°, not a trace of either lead or sulphuric acid could be found. In no case of the action of nitric acid on lead sulphate was lead nitrate formed, as stated by Rodwell (*Chem. Soc. J.*, **15**, 42).

Potassium and sodium nitrates have no action on lead sulphate.

Boric acid and the *borates of potassium* and *sodium* have no action on lead sulphate, either in the cold or at the boiling heat.

Some of the preceding experiments repeated with selenate in place of sulphate of lead, gave analogous results.

In conclusion, it is evident that in the action of acids on salts, and of one salt on another in presence of water, the laws of Berthollet cannot entirely account for all the phenomena which take place. The general conclusion that must be drawn from these experiments, in which two inverse reactions are possible, is that in all cases a particular state of equilibrium is established in a short time, after the attainment of which no further action takes place, so long as the condition of the liquid remains the same. The formation of certain double salts, which are decomposed by water (according to Deville's laws of the dissociation of salts by water), occasionally complicates the reactions, but even in this case, the conditions of equilibrium are but modified, not destroyed.

It may be remarked, finally, that the fact that lead sulphate is attacked by so many salts, and probably by others also, shows that lead cannot be correctly estimated as sulphate, except in the absence of other salts. C. W. W.

Inorganic Chemistry.

Density of Chlorine at High Temperatures. By A. Lieben (*Compt. rend.*, **89**, 353—356).—The abnormal vapour-density of chlorine at 1300° observed by V. and C. Meyer (*Ber.*, **12**, 1426), may be explained without the assumption that chlorine is not an element, but a compound containing oxygen. 1st. It is possible that at a temperature of 700° the coefficient of expansion of this gas is somewhat higher than that of oxygen, nitrogen, &c.; or 2nd, the lower density of the gas may be due to the partial dissociation of the chlorine molecules (Cl_2) into free atoms. If at the temperature at which the experiments were made half the chlorine-molecules split up into atoms, the density of the mixture would be two-thirds of the density of non-

dissociated chlorine-molecules, viz., 23·66. This number is identical with that obtained from the results of Meyer's experiments.

W. C. W.

Action of Potassium Pyrogallol on Nitric Oxide. By G. Lechartier (*Compt. rend.*, **89**, 308—310).—Nitric oxide, NO, is decomposed by potassium pyrogallate, yielding from one-third to one-quarter its volume of nitrous oxide; a small quantity of nitrogen is also liberated. The reaction may be expressed by either of the following equations: $2N_2O_2 = N_2O + N_2O_3$; or $6N_2O_2 = 4N_2O + N_2O_5 + N_2O_3$.

W. C. W.

Production of Sulphur from Sulphurous Acid and Hydrogen Sulphide. By J. Stingl and T. Morawski (*J. pr. Chem.* [2], **20**, 76—105).—In this paper, the authors give an account of their investigation of Schaffner and Helbig's process for the recovery of sulphur from alkali residues. This process depends on the production of hydrogen sulphide by treating the residue with a solution of magnesium chloride; the sulphuretted hydrogen so produced is then brought in contact with a solution of sulphurous acid in presence of an aqueous solution of calcium or magnesium chloride, and thus the sulphur is separated out (Lunge, this vol., 751).

I. *Action of Magnesium Chloride on Calcium Sulphide.*—The first product of the reaction of these bodies at the ordinary temperature is magnesium sulphide, whose aqueous solution on standing becomes turbid owing to formation of a magnesium polysulphide, thus: $5MgS + H_2O + O = Mg_4S_5 + Mg(HO)_2$. When, however, solution of magnesium sulphide is heated, the sulphuretted hydrogen is evolved, with the formation of magnesium hydrate.

II. *Action of Hydrogen Sulphide on Sulphurous Acid in presence of Salts.*—By the action of hydrogen sulphide on a concentrated solution of sulphurous acid, pentathionic acid is formed, which the authors prepare by treating the solution with barium carbonate, filtering quickly, and precipitating the barium in the filtrate with dilute sulphuric acid. Like tetra- and tri-thionic acids, pentathionic acid free from sulphuretted hydrogen gives a black precipitate of lead sulphide when boiled with a potash solution of lead oxide. Further, solutions of alkalis decompose pentathionic acid with separation of sulphur, thus distinguishing it from tetra- and tri-thionic acids; on boiling, sulphite and thiosulphate are formed, thus: (1) $5H_2S_5O_6 + 10KOH = 5K_2S_4O_6 + S_5 + 10H_2O$; (2) $5K_2S_4O_6 + 5S + 18KHO = 7K_2S_2O_3 + 6K_2SO_3 + K_2S_5 + 9H_2O$. Pentathionic acid is oxidised by potassium permanganate to trithionic acid without any manganese precipitate being formed; but on further oxidation, even in presence of sulphuric acid, a brown precipitate of an oxy-manganese compound is formed. Trithionic acid is oxidised to sulphuric acid, but only on boiling and in presence of a considerable excess of sulphuric acid. Pentathionic acid is decomposed but slowly by hydrogen sulphide, sulphur separating out; the decomposition is increased by heat; no sulphuric acid is formed in this decomposition. Solutions of neutral salts have no action on pentathionic acid. The carbonates of the alkalis and alkaline earths have a similar but less energetic action than

the solutions of alkaline hydrates. Calcium carbonate decomposes a solution of pentathionic acid, forming sulphur and calcium tetrathionate; by boiling, this is further decomposed to trithionate, and finally to sulphate and sulphur. If, however, after adding the calcium carbonate, hydrogen sulphide is passed into the solution, then calcium thiosulphate and sulphur are formed. The same result is obtained when aqueous solutions of hydrogen sulphide and sulphurous acid react in presence of calcium carbonate. This reaction is expressed by the equation $CaS_4O_6 + Ca(HS) = 2CaS_2O_3 + S + H_2S$.

By passing hydrogen sulphide into a solution of sulphurous acid in presence of a salt, sulphur always separates out, and in quantities varying from 86—94 per cent. of the theoretical amount. In the filtrate, pentathionic acid could always be detected and also quantitatively proved. The concentration of the sulphurous acid solution influences the reaction; the more concentrated it is, the less is the quantity of sulphur which separates out. Further, the authors have found that potassium and barium salts give a precipitate of plastic sulphur, whilst those of calcium, magnesium, and sodium give a flocculent form of sulphur.

By experimenting with varying quantities of salts, such as chlorides, sulphates, and carbonates, the authors conclude that their action in Schaffner and Helbig's process is entirely a physical one. A solution of sulphurous acid treated with hydrogen sulphide, when examined by the microscope, is seen to contain a number of small, round bodies, which are transparent bubbles of sulphur; these, on adding a salt solution, are destroyed, and the sulphur separates out in flocks.

P. P. B.

Preparation of Sulphuretted Hydrogen. By J. Fletcher (*Chem. News*, **40**, 154).—The plan is to heat in a small glass flask sulphur and solid paraffin, with a few pieces of broken tobacco-pipe, leading the resulting gas, by means of a perforated cork, india-rubber, and glass tube, directly into the solution to be tested. The first gases are not sulphuretted, but when the mixture has been thoroughly fused and mixed, the sulphuretted hydrogen passes over abundantly.

The advantage of the process is, that the moment the flame is removed, the evolution of gas ceases and the little apparatus can be laid aside without fear of creating offensive smells. D. B.

Tetrathionic and Pentathionic Acids. By E. Pfeiffer (*Arch. Pharm.* [3], **14**, 334—344).—The author criticises a paper by M. W. Spring, in the *Bull. Acad. Roy. Belg.*, **45**, and asserts that the existence of pentathionic acid has never been proved; that what has been considered to be penta- is really tetra-thionic acid; that the salt of an acid obtained by Ludwig (*Arch. Pharm.*, **51**, 259) which has the formula $K_4S_9O_{12}$ + Aq, consists of $K_2S_4O_6 + K_2S_5O_6$ + Aq, and that pentathionic acid is incapable of existing free or in the form of a salt in the presence of other salts. E. W. P.

Vapour-densities of some Metallic Chlorides. By V. and C. Meyer (*Deut. Chem. Ges. Ber.*, **12**, 1195—1200).—The vapour-densities of stannous chloride, zinc chloride, and ferric chloride have been

determined by the authors' now well-known method with the following results:

	Found.	Calculated.
Stannous chloride	12·85 at 619°C. 13·08 at 697°	13·06 for Sn_2Cl_4
Zinc chloride	4·53 at 890° 4·61 at 907°	4·70 for $ZnCl_2$
Ferric chloride ..	11·14 at 447° 11·01 at 619° 11·42 at 447° (Deville and Troost) 11·37 at 447° (Deville and Troost)	11·23 for Fe_2Cl_6

As regards stannous chloride, Rieth (*Ber.*, **3**, 668) found numbers for its vapour-density equivalent to 7·47 and 6·88 respectively, the calculated for $SnCl_2$ being 6·53. The authors conclude that this result was due to Rieth having employed a temperature at which the stannous chloride underwent dissociation. In confirmation of this, they find that at a bright red heat the salt evolves chlorine.

At a temperature of 697°, ferric chloride and likewise aluminium chloride evolve chlorine. On heating ferrous chloride in an atmosphere of nitrogen it is decomposed into ferric chloride and metallic iron: hence the determination of the vapour-density of this substance presents great difficulties.

Note by the Abstractor.—The results obtained above for stannous chloride do not finally settle its molecular formula, for the determinations of its vapour-density were made at temperatures (619° and 697°) too near its boiling point, this latter having been found by Williams and Carnelley (*Chem. Soc. J.*, 1879, 563) to be 617—628°. This is probably the true explanation of the lower number found by Rieth, and which corresponds to the simpler formula $SnCl_2$. T. C.

Constitution of Ultramarine. By R. Rickmann (*Dingl. polyt. J.*, **232**, 164—176).—Most chemists regard ultramarine as a sodio-aluminic silicate and a sulphur-compound, and it is assumed, that on the composition of the latter depends the difference of colour, which ultramarine gives (white, green, blue, red, and yellow). The great variety of opinion as to the hypotheses of the formation and composition of the different ultramarines, may be explained by the variable and irregular composition of artificial ultramarine. This varies in accordance with the mode of preparation and the composition of the raw materials—a circumstance which explains why ultramarine, when prepared on a large scale, does not possess the degree of purity which would enable chemists to draw conclusions by chemical analyses as to the constitution of ultramarine.

In the present paper a different mode of investigation has been pursued. In the first place, the composition of white ultramarine was ascertained. This could be done by analysis, as this substance has a uniform composition. The conditions of changes from white to green and blue were then noted, and from the results conclusions were drawn as to the constitution of blue ultramarine. It was found that in the blueing process a succession of complicated reactions takes place,

which renders it impossible to deduce the composition of blue ultramarine from the results of analysis.

I. *White Ultramarine.*—A large number of experiments was undertaken, which proved that white ultramarine is a compound of sodioaluminic silicate and sodium monosulphide. Although Hoffmann has shown that the silicate in white ultramarine rich in silica differs in composition from that in white ultramarine poor in silica, the author shows that Hoffmann's ultramarine rich in silica does not exist; by heating 1 mol. of clay with 1 mol. of silica and 1 mol. of soda, a double silicate, of the formula $Na_2Al_2Si_3O_{10}$, is obtained, which, when ignited with 2 mols. of Na_2S, should give Hoffmann's white ultramarine rich in silica ($Na_2Al_2Si_3O_{10} + 2Na_2S$). However, a dark-blue ultramarine is obtained, which shows that the excess of silicic acid combined with aluminic silicate, acts directly on the sodium monosulphide; the silicate in both ultramarines, therefore, must be the same. From these observations and a large number of analyses made by Rickmann, Hoffmann, and Lehmann, the author assigns to white ultramarine the formula $(Na_2Al_2[SiO_4]_2)_2.Na_2S$.

II. *Blue Ultramarine.*—White ultramarine is converted into the blue by roasting with addition of sulphur (blue-burning), the white being transformed rapidly first into green and then into blue. Gentele has already shown that the blueing properties of green ultramarine are due to the formation of sulphurous acid; and Ritter mentions, with regard to the mode of action of this acid, that during the blue-burning, a certain quantity of the corresponding sodium-salts is produced. Although this fact has been disregarded by chemists, the author shows that by the quantity of the sodium-salts formed we may obtain the means of pursuing and explaining the blueing process. The question whether in the formation of blue, the sodium is taken from the sulphide or the silicate, is answered by the statement that the blueing agent withdraws the sodium from the silicate and not from the sulphide present in white ultramarine. The blueing process can only be explained by assuming the presence of sodium sulphosilicate. The following facts afford further proof of the correctness of this assumption, (1) in the blueing process only small quantities of sulphuretted hydrogen are expelled; (2) when gaseous hydrochloric acid forms the blueing agent, water is formed and also sodium chloride, but no hydrogen; (3) when anhydrous acids are used, the corresponding sodium-salts are obtained.

If, according to other hypotheses, the conversion into blue depends on the formation of sodium polysulphide, this conversion should also be brought about by other means which cause the formation of polysulphides. It is known that a polysulphide is formed from a monosulphide both by withdrawal of sodium and addition of sulphur; thus ultramarine should be converted into blue by treatment with sulphur. This is, however, impossible; by roasting white ultramarine with sulphur and excluding the air, blue ultramarine cannot be produced.

After criticising Lehmann's explanation of the blueing process, the author concludes his paper with the following statements. Artificial blue ultramarine is not to be regarded as a chemical individual, but as

a mixture of various compounds, one of which must be considered as essential to its constitution, whilst the others may be regarded as contaminating bye-products. Sodium sulpho-silicate in combination with aluminic silicate represents the essential compound. Whether the latter is necessary to the constitution of blue ultramarine, or whether it acts as a means of transferring silicic acid could only be ascertained if it were possible to obtain blue ultramarine perfectly free from alumina.

Blue ultramarine in its purest form, therefore, is a sodio-aluminic silicate, in which sodium oxide is replaced by sodium sulphide.

Sodic aluminic silicate .. $Na_2OSiO_2.Al_2O_3SiO_2 = Na_2Al_2(SiO_4)_2$
Blue ultramarine $Na_2SSiO_2.Al_2O_3SiO_2 = Na_2SiO_2S.Al_2SiO_5$.

D. B.

Formation of Crystalline Metallic Oxides by means of Potassium Cyanide. By L. Varenne (*Compt. rend.*, **89**, 360—361).—Stannous oxide may be obtained in the form of a violet-black crystalline powder by boiling for several days with excess of potassium cyanide the precipitate which is produced by the addition of potassium cyanide to the solution of a stannous salt.

Pure oxide of antimony could not be prepared by an analogous process. W. C. W.

Zinc Phosphates. By W. Demel (*Deut. Chem. Ges. Ber.*, **12**, 1171—1174).—*Acid phosphate of zinc*, $ZnH_4(PO_4)_2 + 2H_2O$, is obtained by dissolving zinc oxide in an excess of aqueous phosphoric acid, 100 grams of which take up about 10 grams of zinc oxide. The clear solution on standing for a few hours deposits large triclinic crystals, which are permanent in the air. Measurements of these crystals are given. The compound loses 1·15 to 1·86 per cent. H_2O at 100°, and dissolves easily in hydrochloric acid; treated with alcohol or ether it remains unchanged. If mixed with 2 to 3 vols. of water it is decomposed, owing to loss of phosphoric acid, and a white crystalline powder remains which is insoluble in water, but soluble in dilute hydrochloric acid. This product has the composition $10ZnO.4P_2O_5.10H_2O$; it loses about 1·6 per cent. of water at 100° and 10·03 per cent. at 280°, without, however, undergoing any visible change. The former of these compounds appears to be the acid phosphate of zinc which is used for dental purposes. T. C.

Compound of Chromic Acid with Potassium Fluoride. By L. Varenne (*Compt. rend.*, **89**, 358—360).—By boiling a concentrated solution of potassium dichromate with hydrofluoric acid, octohedral and cubical crystals are obtained, which have the composition $KF1.2CrO_3$. The salt may be recrystallised from a small quantity of water, but is decomposed if a large excess of water is used. The crystals are efflorescent and attack glass. They are decomposed by sulphuric acid, hydrofluoric and chromic acids being liberated. Treated with alkalis, they yield potassium fluoride and an alkaline chromate. W. C. W.

Presence of Nitrogen in Steel. By A. H. Allen (*Chem. News*, **40**, 135).—The method adopted for indicating the presence of nitrogen in steel was to dissolve the steel in hydrochloric acid, by which means any combined nitrogen may be presumed to be converted into ammonia. The solution obtained was then distilled with excess of lime, and the distillate examined for ammonia by Nessler's method. Very special precautions were taken to obtain the hydrochloric acid and other materials free from any trace of ammonia or nitrous compounds, and the air was entirely expelled from the apparatus before commencing the operation. The addition of Nessler's solution after taking these precautions caused a very marked yellowish-brown coloration. On comparing the tint produced with that yielded by a dilute solution of ammonium chloride of known strength, results were arrived at representing the proportions of nitrogen present in various typical specimens of steel.

The author regards these results as preliminary merely, and proposes to extend the research to various classes of steel and iron, and especially to such specimens as have been found to possess anomalous characters. Of these characters the evolution of ammonia from freshly-fractured surfaces is among the most striking. D. B.

Mercuric Chloriodide. By H. Köhler (*Deut. Chem. Ges. Ber.*, **12**, 1187—1191).—Liebig (*Schweiger Journ.*, **49**, 252) obtained a white crystalline body, having the composition $2HgCl_2 + HgI_2$, by saturating a boiling solution of mercuric chloride with mercuric iodide, and allowing the liquid to cool. Boullay (*Ann. Chim. Phys.*, **34**, 340), and also Larrocque (*N. J. Pharm.*, **4**, 15) by a similar method obtained a yellow powder, $HgCl_2 + HgI_2$, which soon became red owing to separation of mercuric iodide. By boiling calomel with an excess of iodine and much water, Selmi (*L. Instit.*, 1844, No. 523) and also Riegel (*Jahbr. f. prakt. Pharm.*, **11**, 396) prepared a chloride in the form of yellow needles, which on keeping assumed a red colour. The author confirms the above results of Boullay, but finds that the red powder resulting after some days' keeping was perfectly homogeneous and crystalline under the microscope, and on analysis gave numbers corresponding with the formula HgClI, or $HgCl_2 + HgI_2$. Boullay's method, however, gives but a poor yield; a better method of obtaining the compound is to dissolve mercuric iodide or iodine in mercuric chloride under pressure in sealed tubes at 160°.

Mercuric chloriodide forms beautiful yellow (rhombic) or bright red (tetragonal, α-P.0P) crystals, with a bluish reflection. It becomes citron-yellow at 125°, and melts at 153° to a golden-yellow liquid. It boils at 315°, and sublimes unchanged at a somewhat lower temperature. It is very sparingly soluble in water, but rather soluble in hot alcohol. By chlorine, it is converted into $HgCl_2$ with development of heat; it may be sublimed in a current of hydrochloric acid, sulphurous anhydride, or sulphuretted hydrogen without decomposition, but in dry ammonia it falls to a grey powder. It is somewhat soluble in dilute hydrochloric acid, and from this solution sulphuretted hydrogen does not precipitate black mercuric sulphide even when hot,

but a voluminous greenish-yellow precipitate of mercuric sulphochloriodide, Hg_2SClI, which is sensitive to light. T. C.

Action of Heat on Metals in a Vacuum. By T. A. Edison (*Chem. News*, **40**, 152—154).—In the course of his experiments on electric lighting the author developed some striking phenomena arising from the heating of metals by flames and by the electric current, especially wires of platinum and of platinum alloyed with iridium.

The first fact observed was that wires of platinum lost weight when heated in a hydrogen flame, the metal colouring the flame green. As to the loss of platinum when heated by the electric current a wire weighing 343 mgms. was kept moderately incandescent for nine consecutive hours, after which it weighed 301 mgms., showing a total loss of 42 mgms. A platinum wire twenty-thousandths of an inch in diameter was wound in the form of a spiral one-eighth of an inch in diameter and one-half an inch in length. The two ends of the spiral were secured to clamping posts, and the whole apparatus was covered with a glass shade $2\frac{1}{2}$ inches in diameter and 3 inches high. Upon bringing the spiral to incandescence for twenty minutes, that part of the globe in line with the sides of the spiral became slightly darkened; in five hours the deposit became so thick that the incandescent spiral could not be seen through the deposit. This film, which was most perfect, consisted of platinum. This loss in weight, together with the deposit on the glass, presented a very serious obstacle to the use of metallic wires for giving light by incandescence, but this was easily surmounted after the cause was ascertained. The wire forming the spiral was coated with magnesium oxide. This spiral was then covered with a glass shade and brought to incandescence for several minutes, but, instead of a deposit of platinum on the glass, magnesium oxide was deposited. From this and other experiments the author was convinced that this effect was due to the washing action of the air upon the spiral, also, that the loss of weight and the coloration of the hydrogen flame were also due to the wearing away of the surface of the platinum by the attrition produced by the impact of the stream of gases upon the highly incandescent surface, and not to volatilisation, as commonly understood.

The author observed in another experiment that a short length of platinum wire one-thousandth of an inch in diameter, held in the flame of a Bunsen burner, will fuse at some part, and a piece of the wire will be bent at an angle by the action of the globule of melted platinum. With a wire four-thousandths of an inch in diameter this effect does not take place, as the temperature cannot be raised to equal that of the smaller wire, owing to the increased radiating surface and mass. After heating, if the wire be examined under the microscope, that part of the surface which has been incandescent will be found covered with innumerable cracks. If the wire be heated to incandescence by the passage of an electric current, the cracks will be so enlarged as to be seen by the naked eye; the wire under the microscope presents a shrunken appearance, and is full of deep cracks. The author explains the cause of this shrinking and cracking of the wire by the expansion of the air in the mechanical and physical pores

of the platinum, and the contraction upon the escape of the air. With platinum or any other metal, the air-spaces may be eliminated and the metal made homogeneous by a very simple process, which is based on the following experiments:—A large number of platinum spirals, all of the same size and from the same quality of wire, were made; each spiral presented to the air a radiating surface of three-sixteenths of an inch; five of these were brought by the electric current up to the melting point, the light was measured by a photometer, and the average light was equal to four standard candles for each spiral just at the melting point. One of the same kind of spirals was placed in the receiver of an air-pump, and the air exhausted to 2 mm.; a weak current was then passed through the wire, to slightly warm it for the purpose of assisting the passage of the air from the pores of the metal into the vacuum. The temperature of the wire was gradually augmented at intervals of ten minutes until it became red. Afterwards the current was increased at intervals of fifteen minutes. Before each increase, the wire was allowed to cool, and the contraction and expansion at these high temperatures caused the wire to weld together at the points previously containing air. In one hour and forty minutes this spiral had reached such a temperature without melting that it was giving a light of twenty-five standard candles, whereas it would undoubtedly have melted before it gave a light of five candles had it not been subjected to this process. On examining this spiral by the aid of a microscope no cracks were visible; the wire had become as white as silver, and had a polish which could not be given it by any other means. The wire had a less diameter than before treatment, and it was exceedingly difficult to melt in the oxy-hydrogen flame. As compared with untreated platinum it was found that it was as hard as the steel wire used in pianos, and that it could not be annealed at any temperature.

The author's experiments with many metals treated by this process have proved to his satisfaction, and he has no hesitation in stating that what is known as annealing of metals to make them soft and pliable is nothing more than the cracking of the metal. In every case where a hard drawn wire had been annealed, a powerful microscope revealed myriads of cracks in the metal. By the aid of a Sprengel mercury pump the author has been able to produce higher exhaustion, and has, by consuming five hours in excluding the air from the wire and intermitting the current a great number of times, succeeded in obtaining a light of eight standard candles from a spiral with a total radiating surface of one thirty-second of an inch, or a surface about equal to one grain of buckwheat. With spirals of this small size, which have not passed through the process, the average amount of light given out before melting is less than one standard candle.

These experiments are still in progress. D. B.

Mineralogical Chemistry.

Distribution of Copper in Primordial Rocks and in the Sedimentary Deposits derived from them. By L. Dieulafait (*Compt. rend.*, **89**, 453).—Copper is uniformly disseminated through all the primordial rocks in such proportion that 100 grams of rock will always give the reactions of copper. It also exists in all the ordinary sedimentary rocks derived from primordial rocks.

Copper has been found in the ashes of various sea-weeds, but has never been directly detected in sea-water. When sea-water, however, is left to evaporate in natural or artificial basins, the black, sulphurous mud which is deposited always contains copper. It is the same with the black marls which accompany gypsum.

The water of the Mediterranean contains copper to the extent of 0·01 gram per cubic meter. It follows from these facts that copper minerals have always been formed during the evaporation of sea-water. They must, therefore, always occur associated with the *débris* of the rock from which the copper was obtained, and also with the various organic and mineral substances which accumulate during the spontaneous evaporation of sea-water. The water derived from primordial rocks should also contain copper, and this has been confirmed by the researches of Filhol and Garrigou on the waters of the Pyrenees, and by those of the author on the waters of Orezza in Corsica.

C. W. W.

Composition of a Nodule of Ozokerite found at Kinghorn-ness. By W. J. Macadam (*Chem. News*, **40**, 148—150).—The material to which this paper refers was discovered in a nest or nodule at the above place at a depth of 15 feet from the surface of the ground, and imbedded five feet in hard trap rock. The rock was sound, no crack or fissure being observable for several feet round the nest. At a point some distance below the nodule, the section shows a series of small veins or fissures running through the rock in various directions and averaging three-quarters of an inch in breadth. On treating a pulverised sample of this rock with hydrochloric acid, 29·73 per cent. of the substance dissolved, whilst the insoluble portion gave after fusion with a flux 70·24 per cent. of soluble substance. The nodule, when broken, consisted of an outer coating of hard rock, an inner lining of calcite crystals, and a centre nodule of bituminous matter. The nodule has a distinct bituminous odour, is a lustrous black, amorphous, soft, solid, easily cut with the nail, and pliable between the fingers. Its specific gravity is ·970; it fuses at 176° F., and becomes solid on cooling. Water and ordinary acids do not act on it. Alcohol has a very slight solvent power, but ether dissolves a large quantity, giving a brown solution, which shows a fine iridescent green colour, when viewed by reflected light. Turpentine dissolves the nodule with a deep brown-black colour. Its analysis gave:—

	Per cent.
Volatile organic matter	99·38
Ash or mineral matter	0·61

26·57 grains were distilled at a bright cherry-red heat and gave :—

	Grains.		Per cent.
Volatile matter	15·93	=	59·955
Fixed carbon	10·48	=	39·431
Ash (mineral matter) ..	0·16	=	0·610

The coke left behind after this treatment was a hard, black, shining, porous mass, and the ash obtained, by incinerating it, was pure white, and consisted principally of calcium carbonate and silica. From the results of the destructive distillation of the nodule, it is seen that the bituminous-like matter consists of a member or members of the olefine series of organic compounds, a point which is further strengthened by the fact that the carbon and hydrogen are contained in the original substance in almost exactly the necessary proportions to form an olefine.

It is probable that the source of the contents of the nodule lies in one of the coal or shale-beds abounding in the district, and that a low internal heat has dissolved the material from its parent stratum.

D. B.

Composition of Pyropissite. By H. Schwarz (*Dingl. polyt. J.*, **232**, 465—476).—This substance is often found in lignite and gives it a light colour; it is known by the low specific gravity and the bright shining flame produced when burnt, and the tar obtained on distillation being rich in paraffin. The author succeeded in extracting this substance from the lignite by means of solvents, but with difficulty, owing to its sparing solubility. The raw material dried in the air showed :—

Hygroscopic water	20·86
Ash	10·88
Organic	68·26

Dried at 100° the substance gave 13·89 per cent. ash. The organic portion contained C = 74·19, H = 11·46, O = 14·35. The ash gave—

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	H_2SO_4.	$CO_2.P_2O_5$ and loss.
60·48	28·63	6·96	2·12	1·81

In accordance with the different solvents used substances were obtained which differed from one another in composition and in the temperature at which they solidified. The following products were obtained :—

	Cold petroleum.	Ether.	CS_2.	Hot petroleum.	Hot alcohol.
C	79·87	80·07	77·84	77·95	78·24
H	13·16	13·20	12·64	12·62	12·45
O	6·97	6·73	9·52	9·43	9·31
Crystallising point	82°	82°	79—80°	79—80°	79—80°

This variation is explained by assuming that these substances are anhydrides of the same acid differing with the solvents used. By

treatment with alcohol containing potash or soda, larger quantities of this substance are extracted, a body being obtained whose composition is much more constant. Its melting point is 150°, and it shows all the properties characteristic of a soap. Acids separate from this soap an organic acid in a gelatinous form, which, when redissolved in hot alcohol, or better in light petroleum, and allowed to cool, crystallises in the form of small, white warts, which, under the microscope, show indistinct crystalline needles. When fused the acid solidifies at 76°. The air-dried acid recrystallised from petroleum (I), alcohol (II), and ether (III) gave—

	I.	II.	III.
C	76·20	75·95	75·89
H	12·65	12·69	12·31
O	11·15	11·36	11·80

The simplest formula calculated from these numbers is $C_9H_{18}O$, which resembles the formula of stearic acid, $C_{18}H_{36}O_2$, and may be regarded as sesquistearic acid. However, as it approaches wax in property, insolubility, and appearance, the author preferred to connect it with cerotic acid, and therefore called this acid oxycerotic acid. It may be supposed that the substances extracted by neutral solvents from pyropissite are anhydrides of oxycerotic acid, from which it is formed when boiled with aloholic potash by absorption of water—

$$C_{27}H_{54}O_3 - H_2O = C_{27}H_{52}O_2, \text{ and } 2C_{27}H_{54}O_3 - H_2O = C_{54}H_{106}O_5 = \begin{matrix} C_{27}H_{53}O_2 \\ C_{27}H_{53}O_2 \end{matrix} \Big\} O.$$

The latter compound may also be regarded as a combination of anhydride with acid. $C_{27}H_{52}O_2$ differs from cerotic acid only by 2H.

By distilling crude pyropissite with superheated steam, a distillate is obtained which solidifies at 55° to 56°, and therefore corresponds with the distillate from the pure acid. This product when purified gave the anhydride of the formula $C_{54}H_{106}O_5$. Solidifying point 77°. By redistilling the first distillate and purifying it with petroleum a wax solidifying at 71° was obtained. The formation of this substance, which contains more paraffin and is probably also formed by distilling pure oxycerotic acid, may be explained by the fact that $2C_{27}H_{54}O_3$ split up into $3(C_{17}H_{34}O) + CH_4 + CO_2 + H_2O$.

On account of the difficulty of obtaining oxycerotic acid in a pure form, its application in the soap and candle industries has not yet been successful.

In conclusion, the author mentions that concentrated sulphuric acid can be used for bleaching only such hydrocarbons as contain but traces of combined oxygen, as is observed in a marked manner in the purification of ozokerite. Although the oxygen is less is this substance than in pyropissite, it is greater than in paraffin, and it is due to this fact, that in bleaching ozokerite with sulphuric acid, much of it is decomposed. D. B.

Barcenite, a New Antimonate, from Huitzuco, Mexico. By J. W. Mallet (*Amer. J. Sci.*, **16**, 306).—This mineral occurs in masses,

weighing more than half a kilogram, having a columnar structure, with long, blade-like, imperfectly developed prisms; they resemble stibnite and livingstonite, from the latter of which this mineral has probably been formed by oxidation. Barcenite is brittle; its fracture is tolerably even; cleavage imperfect, parallel to one prismatic face; hardness = 5·5; specific gravity, when freed from air, = 5·343 at 20°. Lustre dull, earthy, inclining to resinous or pitch-like; opaque; very dark grey or nearly black; streak ash-grey, with a slight greenish tinge; faces of the pseudomorphous crystals sometimes covered with red pulverulent cinnabar or with yellowish-white antimony ochre.

When heated, barcenite gives off water, mercury, mercuric sulphide, and a little oxide of antimony; with reducing agents, a bead of metallic antimony is obtained.

The mineral is totally insoluble in either hydrochloric or nitric acid, and is but very slightly dissolved by boiling ammonium sulphide. A strong boiling solution of soda dissolves a small quantity of antimony. Hydrogen at a red heat gives metallic antimony and mercury. Analysis gives the subjoined numbers:—

S.	Hg.	Ca.	Sb.	O.	H_2O (constitutional).	H_2O (below 130°).	SiO_2.	
2·82	20·75	3·88	50·11	17·61	3·50	1·23	0·10	= 100·00

The whole of the sulphur exists as mercuric sulphide. The mineral is apparently a mixture of mercuric sulphide, antimonic acid, and an antimonate of calcium, mercury, and triad antimony of the formula $\left.\begin{matrix}(R''O)_4\\ Sb_2O_3\end{matrix}\right\}.(Sb_2O_5)_5$.

The natural antimonates may be formulated as follows (Sb = 120):—

Monimolite	$(R''O)_4.Sb_2O_5$
Romeite (Mallet)	$(R''O)_6.(Sb_2O_3)_3.(Sb_2O_5)$
Romeite (Dana)	$(R''O)_3.Sb_2O_3.Sb_2O_5$
Ammiolite	$(CuO)_3.Sb_2O_5$
Mineral from Chili (Rivot)	$(CuO)_5.(Sb_2O_3)_3.(Sb_2O_5)_3$
Barcenite	$(R''O)_4.(Sb_2O_3).(Sb_2O_5)_5$

It will thus be seen that all of them are of a basic character except the last, which is acid. C. W. W.

On a Pseudomorph after Anorthite, from Franklin, New Jersey. By W. T. Rœpper (*Amer. J. Sci.* [3], **16**, 364).—These crystals are found either in detached pieces or in a stratum of limestone, accompanied by sphene and hornblende; they are from one-eighth to two or three inches in length, and the faces are covered with minute prismatic crystals.

The crystals are distinctly felspathic in habit, the prevailing faces in the order of their dominancy being 0P, $\infty\breve{P}\infty$, ∞P, $2\breve{P}\infty$, $2\bar{P}\infty$, P. Angle 0P : $\infty\breve{P}\infty$ over $2\breve{P}\infty$ = 85° 38′; 0P : ∞P′ = 114° 32′; ∞P : ∞P′ = 120° 50′. Cleavage parallel to 0P and $\infty\breve{P}\infty$ easy and distinct, generally dull; basal cleavage occasionally sub-pearly. Hardness = 6; sp. gr. 3·06—3·10; colour bluish-green to greenish-white.

Fusible with some difficulty to a slightly vesicular glass. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	Loss on ignition.
39·73	32·53	2·80	1·44	14·93	0·43	5·01	3·65 = 100·52

The magnesia is probably too high, which would make the oxygen ratio 21·19 : 16 : 5·23, that of anorthite being 4 : 3·1.

The mineral appears to have undergone alteration, as evidenced by its microscopical structure, which is that of a congeries of small crystals; the change probably consists in a re-arrangement of some of the constituents and the introduction of some potash and water.

Note by J. D. Dana.—Hawes (*Mineralogy and Lithology of New Hampshire*) mentions some altered crystals of anorthite, in which the removed calcium is not replaced by alkali, but almost all lost.

C. W. W.

Composition of Slate. By E. Maumené (*Compt. rend.*, **89**, 423).—According to all published analyses, slate is a silicate of aluminium and iron, containing a little magnesia but no carbonates. This composition does not account for the alteration which slates undergo on exposure to air, or for the action of acids on them.

Three specimens of slate gave the following percentages of calcium carbonate:—Slate from Angers, 0·051; La Chambre (Savoy), 0·275; Lavagna (Italy), 0·537. The great value of the Angers slate is thus demonstrated.

C. W. W.

Experiments on the Erosive Action of Strongly Compressed Hot Gases with Reference to the History of Meteorites. By A. Daubreé (*Compt. rend.*, **89**, 325—330).—The very hot and strongly compressed gases, given off by the explosion of nitroglycerol or dynamite, perforated a spherical mass of wrought iron with numerous circular holes, which were in many instances surrounded by a projecting rim of the displaced metal, as if they had been made with a punch.

W. C. W.

Curious Concretion Balls derived from a Colliery Mineral Water. By T. Andrews (*Chem. News*, **40**, 103).—The water on which these observations were made was collected from the "sump" of the Wortley Silkstone Colliery, the samples being obtained during typical dry and rainy seasons. The water had percolated from the surface a distance of 35 yards through strata. Several analyses of this water made at various times indicate that the chief mineral constituents present in the water are iron, calcium, and magnesium, in the form of sulphates. The water shows an acid reaction to litmus, and quickly throws down a copious ochreous deposit when heated. Some curious balls of mineral matter are occasionally found in the feed-tank of the colliery boilers which are supplied with this water. The water in this tank has an average temperature of 164° F. These balls are no doubt formed from the deposit thrown down when the mineral water is heated. The action of steam playing on the surface of the water probably causes circular eddies, and when a nucleus has thus been formed

it is easy to conceive of the gradual formation and consolidation of these balls.

The following is the analysis of the balls and also of the residue deposited in the boilers, from which it will be seen that the balls are quite different in composition, owing probably to the difference in the temperature between the feed-tank and the boiler.

Boiler deposit.	Per cent.	Concretion balls.	Per cent.
Moisture	6·85	Moisture	2·30
Combined water, organic matter	5·80	Loss on ignition, organic matter, &c., contains matters extracted by ether, 5·8 per cent.	24·40

	SiO_2.	Fe_2O_3, Al_2O_3 and P_2O_5.	$CaSO_4$.	MgO.
Boiler deposit	1·80	6·10	78·55	0·65

	SiO_2.	Fe_2O_3.	Al_2O_3.	P_2O_5.	CaO.	MgO.
Concretions	1·80	62·86	5·43	2·81	0·40	trace

Observations were made to ascertain the temperature at which the deposit and turbidity take place. In dry seasons, the turbidity commences at 147° F., in wet seasons at 160·5° F. D. B.

Organic Chemistry.

Vapour-densities of Certain High-boiling Organic Compounds. By L. Troost (*Compt. rend.*, **89**, 351—353).—The determinations of the vapour-density of the following substances, which were made under the ordinary and under diminished pressure (varying from 141 to 260 mm.) gave concordant results.

	Temperature.	Vapour-density observed.	Vapour-density calculated.
Phthalic anhydride	B. p. of mercury.	5·23 —5·28	5·13
Resorcinol	„	3·807—3·89	3·81
Ethyl benzoate	261°	5·51 —5·55	5·2
Amyl benzoate	280°	6·69 —6·73	6·65

W. C. W.

Unsaturated Hydrocarbons resulting from the Decomposition of American Petroleum. By L. Prunier (*Ann. Chim. Phys.* [5], **17**, 5—62).—Light petroleum boiling between 50° and 80° was volatilised, and its vapour passed through a red-hot porcelain tube; the products of its decomposition were received in a series of flasks containing bromine, and the unsaturated hydrocarbons absorbed: a kilogram of bromine, representing 1,200 grams of mixed bromides, be-

coming thus decolorised in about five or six hours. The permanent uncondensable gas burnt with a brilliant flame.

By fractional distillation in a vacuum, the mixture was resolved into ethylene, propylene, butylene, and amylene dibromides, together with a difficultly volatile crystallisable body, corresponding with the formula $C_4H_6Br_4$, which was identified as the crotonylene tetrabromide described by Caventou. This substance was in some cases accompanied by a homologue, $C_5H_8Br_4$.

In the distillation of crude petroleum, bromine absorbs nothing from the gas which escapes at the beginning of the operation, but after the temperature has risen considerably, and when the bottom of the retort is nearly or quite red-hot, large quantities of unsaturated hydrocarbons are disengaged. The bromides thus produced are more complex than those obtained from light oils, but the character of the decomposition is essentially the same. The presence of members of the acetylene series was also established.

In order to ascertain whether the crotonylene tetrabromide obtained as before mentioned, which agreed perfectly with the compound prepared by Caventou from the butylene bromide of ordinary amyl alcohol, was identical or not with the ethyl-acetylene derivative of Berthelot, the latter body was prepared synthetically according to Berthelot's directions, and converted into the tetrabromide. The melting point, crystalline form, and other characters of the two compounds were alike, so that there can be no reasonable doubt but that crotonylene and ethylacetylene are one and the same body. The author has also prepared propyl-, butyl-, and amyl-acetylene.

In attempting to reduce propylene dibromide by means of nascent hydrogen, it was found that the yield of propylene was much less than theory indicated, and that a viscid liquid of penetrating odour was produced in notable quantity. This latter body, on examination by fractional distillation, was resolved into two or three liquids, which were proved to be polymerides of propylene. Dipropylene was present in considerable quantity, but the bulk of the liquid was hexpropylene, as far as its boiling point may be taken as indicative of its condensation. In the case of butylene dibromide, the polymerisation was less observable, and the yield of simpler hydrocarbons was more satisfactory.

Petrocene.—The complex product known by this name consists of a mixture of solid hydrocarbons which distil over at high temperatures towards the end of the operation in the rectification of American petroleum. It is of a brilliant green colour, and crystallises like spermaceti. Its density is 1·206. It has no fixed melting point; it softens at 160°, but fusion is not complete under 190°. The finely powdered substance was exhausted with boiling alcohol until nothing further dissolved, when it was found that about one-third had passed into solution. From this liquor, a yellowish-green substance crystallised on cooling, which on examination proved to be chiefly anthracene. The filtered alcoholic solution was afterwards fractionally precipitated by addition of water, but the separate examination of the paraffins so obtained was not undertaken.

The residue insoluble in alcohol was treated with cold ether, which

dissolved out a number of yellow hydrocarbons, consisting of anthracene, pyrene, chrysene, chrysogene, and a new body termed by Fittig fluoranthene. The portion insoluble in ether which had now acquired a magnificent green colour, was soluble in carbon bisulphide and in chloroform. From these solvents a clear yellow substance crystallised on partial evaporation, which was found to be chrysene, melting at 248°. On addition of two volumes of alcohol, a grey substance was precipitated, which, although little soluble in alcohol or ether, was readily soluble in colourless petroleum, upon which it conferred the phenomenon of fluorescence. It consisted of a mixture of quinones, of which chrysene-quinone was the principal constituent. The addition of water to the solution from which the quinones had separated precipitated a mass of hydrocarbons which could be only imperfectly resolved into their constituent paraffins. One was obtained melting at 250°, another at 280°, and a residue melting above 290°. It is possible that these bodies are nothing more than chrysene and chrysogene or allied substances.

By exhausting the green mass insoluble in ether with boiling benzene, and allowing it to crystallise, a mother-liquor is eventually obtained from which alcohol precipitates a white powder. This substance, by treatment with glacial acetic acid, is resolved into a soluble and an insoluble portion. The former on analysis gave numbers corresponding with the empirical formula $(C_3H_2)_n$, to which series chrysene and fluoranthene belong. An examination of its picrate gave the formula $C_{12}H_8$, which is the same as that of acenaphthylene. It is, however, only an isomeride of this hydrocarbon, since it is insoluble in alcohol.

The portion insoluble in acetic acid melted after crystallisation from chloroform or petroleum at 119°. It was very difficult to purify it entirely from the solvent, traces of which it seemed always to retain. The formula $(C_7H_4)_n$ corresponded best with the analytical results.

Carbopetrocene.—The less fusible portion obtained by fractionally crystallising petrocene has been termed carbopetrocene. It begins to melt at 200°, and fusion is complete at 238°. Its colour is of a sombre-green, inclining to brown. By exhausting it with alcohol and petroleum, its percentage of carbon was raised to 97·09—97·12, which agrees nearly with the formulæ $(C_5H_2)_n$ and $(C_6H_2)_n$. Ether removes a notable quantity of pyrene, anthracene, benzerythrene, &c., whilst chloroform dissolves from the residue a brown fluorescent substance (benzerythrene), leaving a red-brown mass (m. p. 305°), which appears green by reflected light. From this, alcohol extracts a yellowish-white hydrocarbon, crystallising in fine silky needles (m. p. 268°). Its analysis agreed with the formula $(C_6H_2)_n$, whilst the examination of its picrate, which is very characteristic, showed that $n = 4$, or $C_{24}H_8$. After having exhausted a hydrocarbon such as carbopetrocene by alcohol, ether, chloroform, acetic acid, and benzene or toluene, there remains undissolved a small quantity, less than one-hundredth of the whole, of a black residue resembling lamp-black. It is nearly pure carbon, containing over 98 per cent. of that element, and is quite insoluble in all ordinary menstrua. J. W.

Physical Properties of Liquid Acetylene. By G. Ansdell (*Chem. News*, **40**, 136—138).—This paper gives a series of accurate determinations of the physical properties of acetylene in the liquid state, and deals with the critical point, the tension of the vapour of the fluid at various temperatures, together with the corresponding densities and coefficients of compressibility. The method of preparing the acetylene gas was by the action of alcoholic potash on dibromethylene, the disengaged gas being collected in the form of the red copper acetylide, from which the gas was obtained by distillation at a gentle heat with hydrochloric acid.

The tension of the vapour of liquid acetylene appears to have been determined by Cailletet, but the results differ entirely from those obtained by the author, one of the reasons appearing to be that, instead of using a carefully calibrated air manometer for determining the pressures, he used the ordinary metallic gauge attached to the pump, which is far from being correct. The formulæ used by the author for calibrating the tubes and also for calculating the volume of the liquefied gas, and the pressure by the air manometer, were those given by Andrews in his researches on carbonic anhydride. It was shown that liquid acetylene has about half the density of liquid carbonic anhydride, and by taking the actual volume of the liquid at − 7° as unity, we obtain (1·264 at + 35·8) 0·00489 as its coefficient of expansion per degree for the total range of pressure; it is therefore only about half as expansible as carbonic anhydride, whose coefficient is 0·01, being but little more expansible than a gas. The apparent compressibility in glass was determined by direct observation, the liquid being forced up in the capillary tube until the latter was completely full, and then the pressure gradually increased, and the diminution of volume read off at intervals of about 10 atmospheres up to about 180 atmospheres. Curves were then plotted, showing the volume at different pressures for the same temperature, and from these the coefficient of compression at any temperature and pressure was easily deduced. From the tables given, it is evident that acetylene is governed by the same laws as other compressible liquids, that is to say, its compressibility increases as the temperature rises, but diminishes as the pressure increases, *e.g.*, at a pressure of 95 atmospheres it is three times as compressible at 35° as at 0° C. D. B.

Solid Cyanogen Hydride. By H. Lescœur and A. Rigaut (*Compt. rend.*, **89**, 310—312).—Pure anhydrous hydrocyanic acid may be preserved for any length of time without undergoing alteration, but on the addition of a small fragment of potassium cyanide the liquid acquires a brown colour, and in the course of a few days solidifies to a black amorphous mass (azulmin), which is frequently mixed with colourless crystals. The crystalline compound may be extracted by means of boiling benzene or ether. It is soluble in alcohol and in boiling water, and has a bitter taste. It dissolves freely in acids, apparently playing the part of a weak base. The hydrochloride is a black hygroscopic mass, and has the composition $(HCN)_3 3HCl + 3H_2O$. The composition of the crystalline hydride is therefore $H_3C_3N_3$.

The black amorphous residue from which the crystals have been extracted by ether is insoluble in the usual solvents. It is a polymeride or mixture of polymerides of the formula $(HCN)_n$. The compound $(CNH)_3.H_2O$ prepared by exposing the solid cyanogen hydride to the action of moisture, or by treating azulmin (derived from aqueous hydrocyanic acid) with warm alcohol, is an amorphous powder sparingly soluble in water, freely soluble in alcohol. It produces a beautiful green coloration in a solution of platinic chloride.

W. C. W.

Action of Zinc Chloride on Normal Butyl Alcohol. By Le Bel and Greene (*Compt. rend.*, **89**, 413).—The authors give in this paper a recapitulation of the results obtained with the lower alcohols of the fatty series, when acted on by fused zinc chloride.

Methyl alcohol gives hexmethylbenzene. A repetition of the former experiments, with purer materials, proves that this is not derived from acetone in the methyl alcohol. Ethyl alcohol gives a semi-equivalent of ethylene and a little aldehyde.

Normal propyl alcohol gives about a semi-equivalent of propylene.

Isobutyl alcohol, $(CH_3)_2 : CH.CH_2.OH$, gives isobutylene, $(CH_3)_2C : CH_2$ (a product of dehydration) and pseudobutylene, $CH_3.CH : CH.CH_3$, but no normal butylene.

Normal butyl alcohol, submitted to the same treatment, gives pseudobutylene and normal butylene, but no isobutylene. It is thus seen that although compounds having lateral chains are easily converted into compounds with continuous chains, the reverse does not seem to take place.

C. W. W.

Methylpropyl Carbinol prepared by Synthesis. By J. A. Le Bel (*Compt. rend.*, **89**, 312—315).—It has been previously pointed out by the author (*Bull. Soc. Chim.*, **22**, 337) that saturated members of the fatty series have the power of rotation, when one of their carbon atoms is united to four different radicles. All naturally occurring compounds follow this law, but several bodies which have been prepared synthetically are inactive, since they consist of a mixture of equal quantities of dextro- and lævo-gyrate isomerides. Methylpropyl carbinol (b. p. 116—120°), $CHMe(OH).CH_2.CH_2.CH_3$, prepared from methylbutyryl by the action of nascent hydrogen, is optically inactive. If sulphuric acid and certain salts are added to the alcohol diluted with twenty times its weight of water, and then a small quantity of *Pencillium glaucum* is brought into the mixture, the dextrogyrate alcohol is slowly consumed, and, on distilling the residue, a lævogyrate alcohol is obtained, 22 c.c. of which produce a rotation of −12·33. In this case the *Pencillium* soon acquires a rose colour. When *Pencillium* is grown on racemic acid, it destroys the dextrogyrate tartaric acid, and in inactive fermentation amyl alcohol, it removes the lævogyrate alcohol.

W. C. W.

Derivatives of Glycerol. By Hanriot (*Ann. Chim. Phys.* [5], **17**, 62—119).—*Monochlorhydrins.*—Instead of preparing these substances by the method originally proposed by Berthelot, which yields but a small product, the author saturates undried glycerol with hydro-

chloric acid gas, and heats the mixture in sealed tubes for 100 hours in a water-bath. The liquid is afterwards gently heated in a vacuum at 100° as long as any hydrochloric acid gas comes off, and finally distilled at 150°. In this manner the tendency to polymerisation is very greatly reduced. The two isomerides are afterwards separated by fractional distillation in the bulb apparatus of Henninger and Le Bel, provided with a special arrangement to avoid changing the receiver during the operation. The apparatus used is illustrated by a woodcut in the original memoir.

The two chlorhydrins exist in very unequal proportions in the mixture. 800 grams were obtained boiling at 139° (α), and 50 grams boiling at 148° (β) under 20 mm. pressure; both had the composition represented by the formula $C_3H_7O_2Cl$. The α-chlorhydrin is colourless, and soluble in ether when free from water and glycerol; it can be distilled under the ordinary pressure when pure, but the presence of the least trace of glycerol causes it to blacken immediately; this reaction is the best that can be made use of to ascertain its purity. Its density is 1·338.

The physical properties of the β-chlorhydrin are the same as those of the α-compound. Its density is 1·328.

In order to determine the constitutional formulæ of these chlorhydrins, some epichlorhydrin was heated with water until it was converted into the corresponding monochlorhydrin; this was found to be identical with the α-compound mentioned above, boiling at 139°. The formula of this chlorhydrin is, therefore, $CH_2Cl.CH(OH).CH_2.OH$, since epichlorhydrin cannot yield the monochlorhydrin with the Cl attached to the middle carbon atom. β-chlorhydrin has, therefore, the formula $CH_2(OH).CHCl.CH_2.OH$. Since allyl chloride in combining with HClO yields the unsymmetrical dichlorhydrin, it was probable that allyl alcohol in combining with the same reagent would produce the chlorhydrin of the formula given above. A compound was obtained in this manner boiling at 145—146° under 20 mm. pressure, which agreed with β-chlorhydrin in all its most characteristic properties. It was further proposed to substantiate the formula of β-chlorhydrin by acting with phosphorus pentachloride on dimethylin, and then to substitute hydrogen for the methyl groupings by the action of hydriodic acid; but in opposition to what is commonly stated, the author found it impossible to prepare dimethylin by the action of sodium methylate on dichlorhydrin, epichlorhydrin being formed instead, from which it appears that sodium methylate acts upon the dichloro-compound exactly in the same manner as caustic soda.

An equally unsuccessful attempt was made to prepare the symmetrical propyl glycol by the hydrogenation of β-monochlorhydrin with sodium amalgam, nothing but condensation-products being obtained.

The zinc-copper couple of Gladstone and Tribe, however, acting on acetobromhydrin, yields a glycol with ease, and in large quantity. The acetobromhydrin is best made by the action of acetic bromide on dry glycerol, those portions being collected which distil between 170 and 180° under 100 mm. pressure. 2 kilos. of this product are dissolved in 3 kilos. of alcohol, and the mixture is poured slowly

upon the coated zinc contained in a flask standing in cold water, a little acid being added occasionally to avoid the formation of flocculent zinc oxide. When the hydrogenation is complete, the liquor is decanted, and the zinc precipitated by the addition of a hot solution of sodium carbonate, the precipitate having been washed with alcohol and the liquors mixed together, potassium carbonate is added to separate the alcohol from the water; the upper alcoholic solution contains nearly all the glycol. From this solution the whole of the water must be separated by means of potassium carbonate, after which the alcohol can be readily separated by distillation. The glycol is best rectified in a vacuum, the distillate being collected until the thermometer has risen to 150°; the quantity obtained by the use of 2 kilos. of bromine is about 130 grams of propyl glycol, boiling at 188°; it is the unsymmetrical variety, apparently pure, or at least containing but traces of the symmetrical glycol.

The action of sodium, silver, and aluminium on α-monochlorhydrin did not give results which were capable of being interpreted; from epichlorhydrin, sodium apparently removes the chlorine, producing a body which, on analysis, gives numbers closely approximating to the formula $C_6H_{10}O_2$. This new body, however, was never obtained in a pure condition, since it combines with, and was never effectually separated from, the sodium chloride formed in the same operation.

Action of Ammonia on Monochlorhydrin.—Negative, or at least unsatisfactory, results only were obtained. 50 grams of pure chlorhydrin were saturated with dry ammonia gas as long as ammonium chloride separated. The liquid was then taken up by ether-alcohol; the latter evaporated; and the residue again saturated with ammonia until no more crystals could be obtained. The body which remained was a yellowish, uncrystallisable, hygrometric syrup, and contained no nitrogen. It was not analysed.

The action of aqueous ammonia on epichlorhydrin is similar to that on monochlorhydrin, since its first effect is to convert the former into the latter. Dry ammonia converts epichlorhydrin into a gelatinous mass, which could not by any treatment be brought into a condition suitable for examination. It is tolerably certain that it contains neither chlorine nor nitrogen, from which it would seem that ammonia acts like caustic potash, removing 2 mols. HCl, and probably producing a 6-carbon body from the union of the two residues of the epichlorhydrin.

Trimethylamine and Monochlorhydrin.—By acting on monochlorhydrin with an aqueous solution of trimethylamine in sealed tubes, a liquid was obtained from which alcohol precipitated a gummy substance, capable of forming a platino-chloride when treated with platinic chloride; the analysis of this salt agreed fairly well with that of the platinum compound of *mono*methyl-glyceramine, from which it would appear that the trimethylamine breaks up into monomethylamine and methyl alcohol; indeed, the presence of the latter body is rendered evident by the formation of methyl chloride during the operation. The liquid from which the monomethyl-compound has been precipitated contains the chloride of trimethyl-glycerammonium, which can be obtained easily as platino-chloride, a form in which it is very stable.

When separated from the platinum by hydrogen sulphide, it occurs as a syrupy unstable liquid, probably containing glycerol, and incapable of being brought into a condition fit for analysis. By treatment with silver oxide, the chlorine can be easily removed; the hydrate, after some days, sets into a solid mass, from which separate crystals cannot be obtained. It has a very alkaline reaction and taste.

Potassium Cyanide and Monochlorhydrin.—There is no difficulty in preparing monocyanhydrin by the action of monochlorhydrin on potassium cyanide, but the compound is eminently unstable, decomposing on distillation even in a vacuum. By boiling the crude product with dilute nitric acid, the cyanhydrin is oxidised; on evaporating to get rid of nitric acid and exhausting the residue with alcohol, a product is eventually obtained as a thick, yellowish, strongly acid liquid, corresponding with butyl-glyceric acid, $C_4H_8O_4$. With the exception of the sodium salt, the salts of this acid are uncrystallisable. It is not precipitated by lead acetate, but its lime salt is precipitable by alcohol from an aqueous solution.

From the manner in which it is formed and from its monobasic character, its constitutional formula is probably

$$COOH.CH_2.CH(OH).CH_2.OH;$$

if so, it should be convertible into malic acid by oxidation. This transformation, however, could not be effected, nothing but acetic and oxalic acids being obtained.

All attempts to prepare *glycide* by the action of potash, lime, silver, or lead oxides on monochlorhydrin were unsuccessful. With baryta, in an ethereal solution, a small quantity of glycide was formed, together with a little epichlorhydrin. When purified as far as possible, it was a colourless, odourless, very mobile liquid, boiling with decomposition between 157 and 160°, and having a density of 1·165 at 0°. When boiled with dilute nitric acid, it is said to be converted into mononitro-glycerol, but no analytical details are given. The nitrocompound is not explosive, but when heated, evolves white vapours and inflames spontaneously; it then burns away with a faintly luminous flame, leaving scarcely any residue. J. W.

Researches on Nitroglycerol. By H. Boutmy (*Compt. rend.*, **89**, 414).—The author finds that in the process of manufacture employed at Vonges, which is founded on the reaction between sulphoglyceric and sulphonitric acids, there is an elevation of temperature of 20° less than in the direct process. If the amounts of heat developed and the quantities of nitroglycerol obtained on washing be measured at different stages of the reaction, it is found that eight-tenths of the heat is developed immediately on mixing the materials, but that traces only of nitroglycerol are obtained on washing with water: and that, on the other hand, 35 per cent. of the nitroglycerol appears to be produced after all development of heat has ceased.

The author attributes this phenomenon to the fact that the nitroglycerol at the moment of production is in an extremely finely-divided state, forming a sort of emulsion, and that in this state it is rapidly decomposed by the water added. The nitroglycerol is not, however,

decomposed by the water itself, but by the acid liquid at a particular degree of dilution; it is unaffected either by concentrated or by very dilute acids.

The following facts are adduced as confirmatory of this theory:—

If the acid mixture is poured into constantly decreasing quantities of water, the yield of nitroglycerol becomes proportionately less until at last nitrous decomposition sets in.

If the nitroglycerol which rises to the top of the mixture be removed, instead of being shaken up again, the yield is increased. The shaking up reduces the nitroglycerol to fine particles, thereby increasing its surface and facilitating decomposition.

If pure nitroglycerol be dissolved in nitric acid, sulphuric acid added, and the mixture instantly poured into water, no nitroglycerol is obtained. If the mixture be allowed to stand before pouring into water, the nitroglycerol is wholly or partially recovered, according to the time allowed. C. W. W.

Ethereal Sulphates of Polyhydric Alcohols and of Carbohydrates. By P. Claesson (*J. pr. Chem.* [2], **20**, 1—34).—The action of sulphuric monochloride on monhydric alcohols gives rise to ethereal sulphates (*J. pr. Chem.* [2], **19**, 231), and a similar reaction takes place with polyhydric alcohols. Thus by dissolving 2 mols. of glycol in small quantities at a time in 1 mol. of sulphuric monochloride, hydrochloric acid is liberated and glycol-disulphuric acid is formed as a thick uncrystallisable liquid, insoluble in ether, and decomposed by heat at 160°. The barium salt, $Ba(SO_4)_2C_2H_4 + 2H_2O$, is prepared by mixing the acid with ice-cold water, and treating the solution with barium carbonate. It crystallises in slender needles; by heating its concentrated solution on a water-bath, it is decomposed with formation of barium sulphate. The potassium salt forms silvery masses consisting of thin prisms; like the other salts, it is insoluble in alcohol; the lead salt is also crystalline, the others are uncrystalline. Glyceryl-trisulphuric acid, $(SO_4H)_3C_3H_5$, is obtained in a manner similar to the above; it crystallises in shining masses, which consist of prisms. The barium salt is obtained by treating the well-cooled aqueous solution of the acid with barium carbonate, and precipitating with alcohol. It at first forms an oil, but after repeated solution in water and precipitation with alcohol, it is obtained as a sandy powder. The acid is decomposed by water, yielding glyceryl-disulphuric acid; when warmed with water, however, it splits up into glycerol and sulphuric acid.

Erythrol dissolves easily in sulphuric monochloride, forming erythrol-tetrasulphuric acid, which crystallises in snow-white masses consisting of small prisms. It is decomposed by water with regeneration of erythrol.

The potassium salt, $(KSO_4)_4C_4H_6 + 4H_2O$, obtained by neutralising the well-cooled aqueous solution of the acid with potash, is sparingly soluble in cold water, but easily in hot water, from which it crystallises in colourless, transparent, hexagonal plates. It loses the water of crystallisation at 100°.

The barium salt, $Ba_2(SO_4)_4C_4H_6 + 4H_2O$, is insoluble in acids and in water. When barium chloride is added to a solution of potassium

erythrol-tetrasulphate, no precipitate forms, but after some time the potassium and barium salts separate out. If, however, the mixed solutions of barium chloride and of the potassium salt are heated in a water-bath, barium erythrol-tetrasulphate separates out in prisms insoluble in acids and in water. Lead erythrol-tetrasulphate is also an insoluble salt, but when solutions of lead acetate and potassium erythrol-tetrasulphate are mixed, no decomposition takes place.

Mannityl-hexsulphuric acid is obtained as an uncrystallisable liquid by dissolving mannitol in sulphuric monochloride. The barium salt, $Ba_3(SO_4)_6C_6H_8 + 5H_2O$, when first prepared is soluble in water, but may be precipitated by alcohol as an oil, which solidifies to a crystalline mass insoluble in acids and water. It is slowly decomposed by sulphuric acid. The remaining salts of mannityl-hexsulphuric acid are soluble in water, and precipitated by alcohol as oily substances, which after repeated precipitations become solid.

The specific rotation of mannityl-hexsulphuric acid determined by means of a strobometer is $[\alpha]_D = +24° 6'$; the mannitol was dissolved in a known quantity of sulphuric monochloride. By determinations with the calcium salt, the value $[\alpha]_D = +25° 6'$ was obtained.

Mannityl-tetrasulphuric acid is obtained by allowing the aqueous solution of the hexsulphuric acid to stand forty-eight hours at the ordinary temperature. Its barium salt is also precipitated by alcohol as an oil, which after repeated treatment with alcohol becomes solid. Determinations of its specific rotation gave the value $[\alpha]_D = +9° 9'$.

Dulcitol dissolves in sulphuric monochloride forming dulcitanpentasulphonic acid, which cannot be obtained crystalline, and which on decomposition with water yields dulcitan. The barium salt, $(Ba_2SO_4)_5C_6H_7 + 3H_2O$, is obtained as a fine powder by precipitating the aqueous solution with alcohol; it has no action on polarised light.

II. *Ethereal Sulphates of Carbohydrates.*—Grape-sugar, dextrin, starch, and cellulose, when dissolved in sulphuric monochloride, all yield a compound crystallising in large, transparent, quadrangular prisms. It is with difficulty freed from impurities, and appears to be dextrose-monochloride-tetrasulphuric acid,

$$CH_2(SO_4H).(CHSO_4H)_3CHCl.CHO.$$

When heated with water it yields dextrose. Grape-sugar dissolved in sulphuric monochloride gave the value $[\alpha]_D = +71° 30'$ as specific rotation; dextrin $[\alpha]_D = +73° 6'$. Whilst the crystalline compound obtained from dextrose and dissolved in water gave $[\alpha]_D = +71° 48'$; that from starch, $[\alpha]_D = +72° 6'$; and that from cellulose gave $[\alpha]_D = +60° 12'$.

Dextrose-tetrasulphuric acid is obtained by treating the above chloride with water; it forms salts easily soluble in water, from which solutions they are precipitated by alcohol as turpentine-like or resinous masses. By continued treatment with alcohol, they may be obtained as sandy powders, which absorb moisture very rapidly. In the dry state they are decomposed at 100°, and even at the ordinary temperature undergo some decomposition.

Dextrose-trisulphuric acid is obtained from the tetrasulphuric acid

by allowing the latter to stand for a day with water at the ordinary temperature. Its salts resemble those of the tetrasulphuric acid, but have a less specific rotation. Its barium salt has the composition $(Ba_4SO_4)_3C_6H_9O_3 + H_2O$. The salts of the tri- and tetra-sulphuric acids are but slowly oxidised by potassium permanganate. They are also decomposed by alkalis with production of sulphates.

Inulin when treated with sulphuric monochloride is converted into levulose, which then forms a compound isomeric with dextrose-monochloride-tetrasulphuric acid. Similarly, cane-sugar is first resolved into dextrose and levulose, and, secondly, ethereal sulphates of these bodies are formed. Milk-sugar is also inverted, dextrose-monochloride-tetrasulphuric acid is formed which crystallises out, and in the mother-liquors galactose-tetrasulphuric acid is formed. Thus Fudakowsky's views that milk-sugar yields by inversion galactose and dextrose, are confirmed. P. P. B.

Methyl- and Dimethyl-diacetonamine. By T. Götschmann (*Liebig's Annalen*, **197**, 27—47).—By the action of ammonia on acetone, Heintz succeeded in preparing the three bases, acetonine, triacetonamine, and diacetonamine (this Journal, **27**, 1080); by an analogous reaction *methyl-* and *dimethyl-diacetonamine* may be obtained. For this purpose acetone, which has been saturated with dimethylamine and has then been left at rest for several days, is mixed with an alcoholic solution of platinic chloride. A double salt of platinum chloride with the hydrochlorides of dimethyldiacetonamine and of dimethylamine, $C_8H_{17}NO.HCl.Me_2HN.HCl.PtCl_4$, separates out as a pulverulent crystalline precipitate. This compound is obtained in yellowish-red crystals by recrystallisation from hot water. In order to separate the dimethylamine from the dimethyldiacetonamine hydrochloride, the platinochloride is decomposed with hydrogen sulphide, and the dimethyldiacetonamine is precipitated from the solution by gold chloride as $C_8H_{17}NO.HCl.AuCl_3$. This compound crystallises in long golden-yellow needles which dissolve freely in hot water.

Dimethyldiacetonamine hydrochloride is a colourless, thick, syrupy, hygroscopic liquid, which solidifies to a crystalline mass when left in a vacuum for several months. On the addition of ether to a solution of the hydrochloride in absolute alcohol, globules of the substance separate out. The solutions of this salt are decomposed by heat, mesityl oxide and dimethylamine hydrochloride being formed. The platinochloride, $(C_8H_{16}NO.HCl)_2PtCl_4$, crystallises in pale-red plates which dissolve in 19 parts of water at the ordinary temperature.

The free base has not been isolated, since dimethyldiacetonamine hydrochloride splits up on the addition of soda into mesityl oxide and dimethylamine. Several salts have, however, been prepared by the action of the corresponding silver salts on the hydrochloride. The *nitrate* forms very deliquescent needle-shaped crystals, which are insoluble in ether and in absolute alcohol. The *sulphate* is a syrupy liquid which can only be obtained in a crystalline state with great difficulty. The *oxalate* is deliquescent. On the addition of ether to an alcoholic solution of this salt, it separates in rhombic prisms.

Action of Methylamine on Acetone.—When an alcoholic solution of

oxalic acid is added to acetone which has been saturated with methylamine, the acid oxalates of methylamine and methyldiacetonamine are precipitated. On evaporating the mother-liquor, an opaque amorphous mass remains, from which an amorphous platinochloride can be obtained of the composition $(C_{13}H_{23}NO.HCl)_2PtCl_4$. Platinum chloride is added to the mixture of methylamine and methyldiacetonamine oxalates; the solution is evaporated in a vacuum, and the residue washed with ether-alcohol. On recrystallisation from hot water, the methylamine platinochloride first separates out, and on slowly evaporating the filtrate, methyldiacetonamine platinochloride, $(C_7H_{15}NOHCl)_2PtCl_4$, is deposited in large rhombic prisms of a pale-red colour. They are soluble in water, but almost insoluble in absolute alcohol.

Methyldiacetonamine platinosochloride, $(C_7H_{15}ON.HCl)_2PtCl_2$, forms dark-red crystals.

Methyldiacetonamine hydrochloride crystallises in very deliquescent needles, which dissolve freely in alcohol. It combines with gold chloride to form the crystalline double salt, $C_7H_{15}NO.HCl.AuCl_3$, which is soluble in alcohol, ether, and hot water. When heated in water to a temperature above 90°, it melts to an oily liquid. The *neutral* and *acid oxalates of methyldiacetonamine* are both crystalline. The former is distinguished from the latter by its hygroscopic nature, and by its being more sparingly soluble in absolute alcohol. The *sulphate* and *nitrate* are thick syrups which cannot be crystallised.

The *picrate* is insoluble in cold water, but it is deposited from a hot aqueous solution in yellow needles which are soluble in alcohol and in ether. W. C. W.

Acids obtained by Distilling the Crude Acids derived from the Saponification of Neutral Fatty Bodies in a Current of Superheated Steam. By A. Cahours and E. Demarçay (*Compt. rend.*, **89**, 331—336).—When the fatty acids obtained by the action of sulphuric acid on neutral fats are distilled in a current of superheated steam, a mixture of hydrocarbons and acids is obtained. The authors consider it probable that these substances owe their origin to the decomposition of oleic acid by heat. These hydrocarbons have been previously described by the authors (*Compt. rend.*, **80**, 1568). To separate the acids from the hydrocarbons, the mixture is dissolved in very dilute soda, and the solution is boiled until the odour of hydrocarbons is no longer perceptible. The liquid is then concentrated and acidified with hydrochloric acid to liberate the acids, which are afterwards separated. By fractional distillation, normal butyric (b. p. 165°), valeric (b. p. 183—185°), caproic (b. p. 202—204°), œnanthylic and caprylic acids were obtained. The two latter appear to be new.*

* Normal caprylic acid appears to be new; but normal œnanthylic acid has been known for several years, having been prepared in 1865 by Schorlemmer, who obtained it by oxidation of normal heptyl alcohol; in 1873 by Grimshaw and Schorlemmer, by oxidation of normal heptyl alcohol and of œnanthylic aldehyde; in 1877 by Mehlis, who likewise obtained it by oxidation of œnanthylic aldehyde; and by Lieben and Janecek, who prepared it by saponification of the cyanide, $C_6H_{13}.CN$, obtained from normal hexyl alcohol. The boiling points and other physical characters of the 7-carbon acids and their ethylic ethers obtained by

Normal œnanthylic acid boils at 221—223°, and solidifies between −13° and −14°, forming pearly leaves. Its sp. gr. is 0·924 at 21°. *Methyl œnanthylate* boils at 172·5—173·5°; its sp. gr. is 0·889 at 18°. *Ethyl œnanthylate* boils at 187—188°; its sp. gr. is 0·877 at 16·5°. *Calcium œnanthylate*, $Ca(C_7H_{13}O_2)_2 + H_2O$, crystallises in pearly needles which are more soluble in warm than cold water, and lose their water of crystallisation at 100°.

Amido-œnanthylic acid, $C_7H_{13}(NH_2)O_2$, is a crystalline compound obtained by the action of ammonia on monobromoenanthylic acid. It forms crystalline compounds with nitric, sulphuric, hydrochloric, and acetic acids.

Normal caprylic acid boils between 239 and 241°, and solidifies at 7°. Its sp. gr. is 0·923 at 17°. *Methyl caprylate* boils at 192—194°; its sp. gr. is 0·887 at 18°. It solidifies to a transparent mass at −48°.

Ethyl caprylate boils at 206—208°, and solidifies at 47°. Its sp. gr. at 17° is 0·878. *Calcium caprylate*, $Ca(C_8H_{15}O_2)_2 + H_2O$, crystallises in slender needles, which are more soluble in warm than in cold water.

Amido-caprylic acid, $C_8H_{15}.(NH_2)O_2$, resembles amidœnanthylic acid in its mode of preparation and its properties. W. C. W.

Japanese Wax. By E. Buri (*Arch. Pharm.* [3], **14**, 403—405).—Japanese wax is a mixture of glycerides, of which palmitin is the principal. A fatty acid, having a higher melting point than stearic acid, appears to be present, but not in large quantities, together with a small quantity of a member of the oleic series. After saponification, one of the fatty acids, produced by decomposition of the soap by an acid, appeared to be soluble in water, and was also soluble in ether and in alcohol. Fractional precipitation with magnesium acetate sufficed to separate the palmitic acid from some other member of the same series, but the quantity obtained of this last was insufficient for analysis. The presence of glycerol was likewise proved by the production of acroleïn, when the concentrated mother-liquor, after separation of the acid, was heated with potassium-hydrogen sulphate.

E. W. P.

Elimination of Bromine from Bromocitraconic Acid, and on a New Organic Acid. By E. Bourgoin (*Compt. rend.*, **89**, 418).—In a preceding paper, the formation of monobromocitraconic acid, by the action of silver oxide on citraconic bromide or citrabromopyrotartaric acid was described. By the action of potash on bromocitraconic acid, the remaining atom of bromine may be removed, potassium bromide being formed, together with a new acid which forms a colourless, syrupy, uncrystallisable liquid having a sour taste, like that of citraconic acid. It is soluble in water, alcohol, and ether. The alkaline salts in aqueous solution give a white precipitate with

these chemists agree very nearly with those of the acid described by Cahours and Demarçay.

	Grimshaw and Schorlemner.	Mehlis.	Lieben and Janecek.
B. P. of acid.....	223—224°	219°	224°
„ of ether	187—188	186—188°	189·3°.

The 7-carbon acid which Tilley obtained in 1841 by oxidation of castor-oil, was doubtless the same acid, though impure.—(Ed.)

silver nitrate, the analysis of which leads to the formula $C_5H_2Ag_2O_4$; the free acid, $C_5H_4O_4$, thus differs from citraconic acid by two atoms of hydrogen. It is also formed by the simple evaporation, at a low temperature, of a solution of bromocitraconic acid, hydrobromic acid being set free, and the new acid formed. If the evaporation of the solution of bromocitraconic acid be effected at a high temperature, carbonic anhydride is given off, and Kekulé's bromocrotonic acid is formed: $C_5H_5BrO_4 - CO_2 = C_4H_5BrO_2$. C. W. W.

Formation of Phenol from Putrefying Albuminoïd Matter. By W. Odermatt (*Bied. Centr.*, **8**, 479).—The author was not able to confirm his original opinion that the phenol was a product of the decomposition of the indole which is found in putrefying albumin, for the presence of indole prevents putrefaction until it has evaporated from the mass. J. K. C.

Synthesis of Phenolglucoside and Ortho-formylglucoside or Helicin. By A. Michael (*Compt. rend.*, **89**, 355—358).—On mixing alcoholic solutions of potassium phenate and acetochlorhydrose, potassium chloride separates out, and on the spontaneous evaporation of the filtrate *phenol glucoside*, $C_5H_6(OC_6H_5)(OH)_4.CHO$, is deposited in long silky needles (m. p. 171—172°). This substance is soluble in water, and the solution is dextrogyrate. It splits up into glucose and phenol when boiled with dilute hydrochloric or sulphuric acid or with potash. The formation of phenol glucoside is represented by the following equation:—

$$C_5H_6Cl(OAc)_4.CHO + Ph.OK + 4EtHO = C_5H_6(OPh)(OH)_4.CHO + KCl + 4EtAcO.$$

In a similar way *helicin* or *orthoformylphenol glucoside*—

$$C_5H_6(OC_6H_4.CHO)(OH)_4.CHO,$$

may be prepared by the action of acetochlorhydrose on potassium salicylite. It forms white needle-shaped crystals, which melt at 175° and decompose at a higher temperature.

By the action of acetochlorhydrose on sodium saligenin, the glucoside of saleritin appears to be formed. W. C. W.

Copaibic Acid. By W. B. Rush (*Pharm. J. Trans.* [3], **10**, 5—6).—To prepare copaibic acid from copaiba, the volatile oil must first be removed, which may be done by distillation in a current of steam, or by one of the following processes:—10 parts of copaiba are dissolved in 10 parts of benzene and well shaken with an equal bulk of soda solution (sp. gr. 1·3), or by mixing 10 parts of copaiba with 10 parts of alcohol and 4 parts of soda solution, when the mixture separates into three layers. The best method, however, is to treat 1 part of copaiba with 8 parts of soda solution, and after the liquid has separated into layers, the volatile oil and alkaline solution are decanted, and the resin which remains is washed with water to free it from traces of alkali. It is then dissolved in benzene, shaken with dilute hydrochloric acid, and the aqueous liquid decanted. The benzene is

evaporated, and the residue which contains the acid is melted over a water-bath, and poured into light petroleum; the solution is filtered, the filtrate evaporated, and the residue melted and poured into alcohol and filtered hot. The resin remains undissolved, and the acid is contained in the filtrate, from which it is deposited in crystals soluble in alcohol, ether, fixed and volatile oils. It gives a crystalline precipitate with an alcoholic solution of lead acetate, and forms a silver compound insoluble in alcohol in presence of a few drops of ammonia. Copaibic acid may also be obtained from the resin by dissolving it in benzene and filtering, the filtrate is evaporated, and the residue heated to 200° F., and treated with pure naphtha and filtered. The filtrate on standing deposits crystals. L. T. O'S.

Maximum Tension and Vapour-density of Alizarin. By L. Troost (*Compt. rend.*, **89**, 439).—The determination of the vapour-density of alizarin is attended with considerable difficulty, inasmuch as at a temperature of 250°, the vaporisation is extremely slow, and at 300° there is considerable decomposition. At these temperatures also alizarin acts on the alkalis of glass, producing a violet compound. The maximum tension of alizarin was found to be 11 mm. at 261°, and 20 mm. at 276°.

Three determinations of the vapour-density in an atmosphere of nitrogen or carbonic acid at 289°, 283·7°, and 292° gave respectively 16·32, 15·0, and 17·8. The formula $C_{14}H_8O_4$ gives a calculated density of 16·62 for a four-volume condensation. The molecule of alizarin in the state of vapour therefore occupies two volumes. C. W. W.

Identity of the Hydrates of Di-isoprene, Caoutchene, and Terpene. By G. Bouchardat (*Compt. rend.*, **89**, 361—364).—When the terpinols obtained by the action of alcoholic potash on the dihydrochlorides of di-isoprene and caoutchene are treated with a mixture of alcohol and nitric acid, they slowly deposit crystalline hydrates, which are identical in composition, melting point (117—121°), and crystalline form (orthorhombic prism 102° 4′) with the hydrate of turpentine oil, $C_{10}H_{16}.2H_2O + H_2O$.

The hydrocarbons, however, are not identical, since oil of turpentine forms a solid monohydrochloride, but caoutchene and di-isoprene do not. The derivatives of the two last hydrocarbons are identical.

W. C. W.

Borneo Camphor. By J. Kachler (*Liebig's Annalen*, **197**, 86—104).—Two samples of genuine Borneo camphor contained respectively 97·7 and 96·5 per cent. of borneol, and from 2·3 to 3·5 parts of resin and other impurities. The borneol was easily obtained in a state of purity by sublimation. The pure compound melts at 197·5—198°, solidifies at 195°, and boils at 212°.

Its specific rotatory power is $[\alpha]_D = +32·7$. Montgolfier found $[\alpha]_D = +37$ (*Ber.*, **10**, 728; this Journal, 1877, ii, 626). The author confirms the observation of Pelouze that ordinary camphor is formed by the action of nitric acid on borneol.

Borneol chloride, $C_{10}H_{17}Cl$, is best prepared by cautiously adding borneol to well cooled phosphorus pentachloride, every precaution

being taken to avoid a great rise of temperature. The mixture is left at rest for two days, and is poured into a large volume of water, when the chloride separates out as a waxy mass. It is purified by recrystallisation from a mixture of alcohol and ether.

Borneol chloride is a colourless substance resembling camphor in appearance; it is somewhat volatile at the ordinary temperature, and has a peculiar odour. It melts at 159° (corr.), not at 147° as previously stated (*Ber.*, **11**, 460), and begins to decompose when heated a few degrees above its melting point.

The chloride is insoluble in water, but dissolves in alcohol and ether. Heated at 95° in sealed tubes with water, it is completely decomposed into hydrochloric acid and a solid camphene, $C_{10}H_{16}$, which melts at 51°, and is dextrogyrate. This hydrocarbon dissolves in alcohol and ether, but is insoluble in water. An addition-product is formed by passing hydrochloric acid into the ethereal solution.

Borneol chloride can also be prepared by heating borneol in sealed tubes at 100° with concentrated hydrochloric acid. The *bromide* is obtained in white crystals (m.p. 75°) by a similar reaction. The author confirms Montgolfier's statement that artificial borneol prepared by Baubigny's method (*Compt. rend.*, **63**, 221) is identical with natural borneol in every respect excepting its action on polarised light. In the preparation of artificial borneol, it is found that the portions formed at the beginning and end of the operation are dextrogyrate, whilst the intermediate portion is lævogyrate.

W. C. W.

Glycyrrhizin. By J. Habermann (*Liebig's Annalen*, **197**, 105—125).—The crystals which are deposited on cooling a solution of commercial "*Glycyrrhizin ammoniacale*" in boiling glacial acetic acid, consist of the acid glycyrrhizate of ammonium, $C_{44}H_{62}NO_{18}(NH_4)$. This body is also contained in the "insoluble glycyrrhizin" of commerce.

After recrystallisation from 90 per cent. alcohol, the salt forms transparent glistening crystalline scales, which are insoluble in ether, but dissolve in hot water. With cold water, the compound forms a transparent gelatinous mass. Lead acetate, silver nitrate, and the salts of the other heavy metals produce a precipitate with solutions of this salt.

Glycyrrhizic acid prepared by the action of sulphuretted hydrogen on the lead salt, resembles dried albumin in appearance. It forms a jelly with cold water, but dissolves in hot water, forming a clear and sticky liquid: it is also soluble in boiling glacial acetic acid, and in warm dilute alcohol. The acid is tribasic. It reduces Fehling's copper solution.

The neutral ammonium salt is a hygroscopic gum-like body, soluble in water and in dilute alcohol.

The neutral potassium salt, $C_{44}H_{60}NO_{18}K_3$, is prepared by warming an alcohol solution of the acid ammonium salt with a slight excess of potash. When the mixture is cold, absolute alcohol is added, which causes the potassium glycyrrhizate to separate out as a resinous mass insoluble in ether and absolute alcohol. The acid potassium glycyr-

rhizate separates out in minute colourless crystals on cooling a solution of the neutral salt in warm acetic acid.

This compound forms a gelatinous mass with cold water, but dissolves in hot water.

Both the neutral and acid glycyrrhizates of ammonium and potassium possess an intensely sweet taste. The barium salt, $(C_{44}H_{60}NO_{18})_2Ba_3$, is amorphous and sparingly soluble. The lead salt forms a sparingly soluble, transparent, brittle gum-like mass. W. C. W.

Active Principle of "Ammi Visnaga." By Ibrahim Mustapha (*Compt. rend.*, **89**, 442).—The author has succeeded in isolating from this plant a crystallisable material, which behaves like a glucoside with cupro-potassic solution. It is a white substance, crystallising in small silky needles, which are very slightly soluble in cold water; much more so in hot water, also in methyl, ethyl, and amyl alcohol, and in chloroform. It is very soluble in ether, and has a bitter taste. It is neutral to turmeric paper. The solution gives with Nessler's reagent a white precipitate soluble in alcohol; and with Loew's reagent a white precipitate soluble in excess.

It exerts an emetic and narcotic action on the animal system.

The author proposes for this glucoside the name *kellin*, from the Arabic name of the Ammi Visnaga. C. W. W.

Lactucarium. By H. Flowers (*Pharm. J. Trans.* [3], **10**, 44—45).—*Lactuca Canadensis* exudes a milk-juice, which in the mature plant is found to contain a bitter principle. The juice collected in September and October is exhausted with hot alcohol and filtered. The filtrate on evaporation yields colourless tasteless needles of lactucerin, a further quantity of which may be obtained by concentrating the mother-liquor and adding water. The clear aqueous solution thus obtained, after being precipitated with basic acetate of lead, treated with sulphuretted hydrogen, and evaporated, leaves a brown amorphous mass of lactucic acid and lactucopicrin.

Lactucerin is soluble in boiling alcohol, light petroleum ether, and chloroform, but only sparingly in cold alcohol; it is insoluble in water. It crystallises in needle-shaped crystals, which melt at 175°, and volatilise when heated more strongly. It is charred by sulphuric acid, but nitric acid has no action upon it.

Lactucin, which has a bitter taste, is nearly insoluble in water, but soluble in alcohol and in acetic acid. It crystallises in scales, and is not precipitated from its solution by ammonia.

Lactucic acid has an acrid bitter taste, and is soluble in alcohol, but insoluble in petroleum spirit, ether, and chloroform; it has a brownish-green colour.

Lactucopicrin forms a brown amorphous mass having a bitter taste, soluble in alcohol, chloroform, ether, and water; it is not precipitated by lead salts.

The residue of lactucarium left after the separation of the above substances was treated with carbon bisulphide and other solvents, but no definite results were obtained.

The statement of Aubergier that the plant is worthless is incorrect,

as it undoubtedly contains several bitter principles with decided physiological action. L. T. O'S.

Gamboge. By D. Costelo (*Pharm. J. Trans.* [3], **9**, 1022).—The value of gamboge consists in the amount of resin it contains, and to ascertain the value of the commercial varieties, samples of lump, pipe, and powdered gamboge were analysed, with the following results:—

10 grams of	Resin. grams.	Gum. grams.	Impurities. grams.	Total. grams.
Lump	6·76	2·74	0·38	9·88
Pipe	7·93	1·945	0·015	9·89
Powder	7·66	2·25	0·07	9·98

The difference between the total weight of the constituents found and that of the substance taken, represents the water which gamboge always contains.

The resin, the so-called *gambogic acid*, $C_{20}H_{23}O_4$, is a reddish-brown translucent brittle substance, soluble in alcohol, ether, chloroform, and carbon bisulphide, and sparingly soluble in petroleum spirit and benzene. Its solutions in alcohol and ether are acid to test papers. It forms salts which are for the most part amorphous precipitates. When boiled with nitric acid it gives a syrupy liquid, which solidifies on cooling. It is soluble in alcohol and ether, and is deposited on evaporation as a yellow amorphous powder.

The gum soluble in water yields when boiled with nitric acid, an amorphous reddish-brown colouring matter, and a colourless crystalline substance. The latter is soluble in water, but insoluble in alcohol, it gives an acid reaction with test papers; the quantity of substance, however, was so small that no satisfactory results could be obtained. On evaporating the solution of the colouring matter in alcohol, a residue of a drab colour is left. It has a bitter taste, and is sparingly soluble in water, but freely in alcohol and ether. L. T. O'S.

Colouring Matter of Palmella cruenta. By T. L. Phipson (*Compt. rend.*, **89**, 316—318).—*Palmella cruenta* is a small blood-coloured algæ, which grows at the base of damp whitewashed walls. In warm and damp seasons it bears a striking resemblance to coagulated blood. A microscopical examination shows that it is composed of minute round cells resembling blood corpuscles. These cells are about 0·004 mm. diameter, and float freely in a mucous liquid, which may be compared to the serum of the blood. They contain a peculiar rose-red colouring matter, which the author proposes to call *palmellin*.

In order to extract this substance, the plant is dried for 36 hours at the ordinary temperature, and is then covered with water. In this way a beautiful rose-coloured solution (orange by reflected light) is obtained, which on evaporation at a temperature not exceeding 40° yields a reddish-blue indistinctly crystalline mass. Palmellin strongly resembles hæmoglobin: like this body, it is insoluble in alcohol, carbon bisulphide, benzene and ether. Its aqueous solution is coagulated by the addition of ammonia, alcohol, or acetic acid, and a precipitate resembling blood fibrin separates out.

The solution coagulates and loses its colour when heated to the boiling point. Ammonium sulphide changes the colour to yellow, and hydrochloric and nitric acids change it to brick-red without coagulating the solution. Salicylic acid destroys the dichroism of the solution, and alters its colour to a blue-violet. Palmellin exhibits one or two absorption-bands between the yellow and green portion of the spectrum. The ash of this body contains iron, calcium, and chlorine.

Colourless rhombic crystals analogous to hæmatin are obtained by adding acetic acid to palmellin.

When a solution of palmellin is exposed to a temperature of 25° for two or three days, decomposition sets in, and the liquid will be found to contain a large number of *vibrions*. W. C. W.

Contribution to the Chemistry of the Pæonia peregrina. By Dragendorff and Stahre (*Arch. Pharm.* [3], **14**, 412—438, and 531—553).—By long and complicated processes, which are fully described, the authors have ascertained the following to be the composition of the *P. peregrina* seeds: moisture, 8·45; ash, 2·57 (containing 0·851 of phosphoric acid); oil (soluble in petroleum spirit), 23·61; resin, together with a small quantity of "indifferent pæony resin," 1·13; tannin, less than 1; pæony fluoresceïn, about 4; pæony brown, about 4; in all, 8·71. Legumin with albumin and mucilage, 5·44; other albuminoïds, and an alkaloïd, 5·5 (N = 1·75); sugar, 1·4; substances insoluble in strong alcohol, but soluble in dilute alcohol and in water, 7·68; arabic acid, 1·22; cellulose, 11·73; other constituents of the cell-walls, 22·56 parts in 100.

In the roots of the same plant are found in addition, glycose, metarabic acid, amylone, calcium oxalate, and pararabin. The age of the root appears to have a very considerable influence on the amount of constituents present.

The alkaloïd found differs from that found in the aconite and diphinium. E. W. P.

Quinine Citrates. By A. F. Mandelin (*Pharm. J. Trans.* [3], **10**, 222—223).—By melting quinine and citric acid together in different proportions and crystallising the salts, the following compounds may be obtained:—

3 mols. of quinine and 2 mols. of citric acid yield a salt having the formula Qu_3Ci_2(Qu = $C_{20}H_{24}N_2O_2$, Ci = $C_6H_8O_{11}$). 1 mol. quinine, and 1 mol. citric acid gave rise to a salt having the formula Qu.Ci.

1 mol. quinine and 2 mols. citric acid give rise to the preceding compound, which Hesse obtained by mixing together 1 mol. quinine and little more than 1 mol. citric acid.

$Qu_2Ci + \frac{1}{2}H_2O$ is obtained by mixing 2 mols. quinine with 1 mol. citric acid.

The solubilities of these three citrates in 100 parts of water are as follows:—

		Cold.	Hot.
Basic quinine citrate,	Qu_2Ci	0·1093	2·25
Neutral „	$Qu_3.Ci_2$.....	0·1133	2·39
Acid „	Qu.Ci	0·1566	2·60

L. T. O'S.

Paricine and Aricine. By O. Hesse (*Pharm. J. Trans.* [3], **9**, 993—994).—This is a reply to a paper by J. E. Howard (*ibid.*, 792) on the cinchona alkaloïds. Paricine occurs in the bark (chiefly in that of the slender branches) of *C. succirubra* from Darjeeling. It is obtained by adding sodium carbonate to a dilute solution of the mixed bark alkaloïds in sulphuric acid until slightly alkaline, and the paricine which is thus precipitated is digested with dilute sulphuric acid at a gentle heat, when the sulphate remains as a yellow mass. This is dissolved in ether, in which it is readily soluble, and light petroleum added to the solution, to precipitate brown-coloured impurities. The pale yellow paricine solution is then poured into light petroleum, and the paricine, which is precipitated, is again treated in the same manner with ether and light petroleum. The paricine thus obtained is a light pale yellow amorphous powder (m. p. 136°), soluble in ether, alcohol, benzene, acetone, and chloroform, but insoluble in water and in pure petroleum spirit; its composition is $C_{16}H_{18}N_2O + \frac{1}{2}H_2O$. Its solution has a bitter taste, a slightly basic reaction, and is optically inactive. It does not neutralise strong acids, but with many acids it forms amorphous salts soluble in excess of the acid; with platinic chloride, it forms a yellow amorphous precipitate, $(C_{16}H_{18}N_2O.HCl)_2 + PtCl_4 + 4H_2O$. Paricine readily decomposes, forming a resinous substance. The brown precipitate mentioned above is a decomposition-product of paricine.

The author is of opinion that there is no relation between paricine and aricine, although Howard states that paricine may be an oxidation product of aricine. Aricine is isomeric with cusconine and cusconidine, and has the formula $C_{23}H_{28}N_2O_4$; by heat it is with difficulty converted into an amorphous alkaloïd which possessss properties totally different from those of paricine. The author considers it probable that the latter body may result from the decomposition of protoquinamicine (obtained by the action of SO_3 on quinamine) thus, $C_{17}H_{20}N_2O_2 + O = C_{16}H_{18}N_2O + CH_2O_2$. The author further asserts that the substance examined by Howard is not aricine, but probably a mixture of homocinchonidine and cinchonidine, or perhaps impure paricine, and moreover, that *C. succirubra* does not contain any aricine.

L. T. O'S.

Quinamine. By A. C. Oudemans (*Liebig's Annalen*, **197**, 48—69).—To prepare quinamine from "quinetum" (a mixture of the various alkaloïds occurring in the bark of *Cinchona succirubra*) the quinine and cinchonidine are precipitated from the slightly acid solution of the hydrochlorides as tartrates. On adding soda to the filtrate, a precipitate is obtained which is dried and exhausted with ether. The ethereal extract contains crude quinamine, which may be separated from cinchonine by recrystallisation from alcohol. The question whether $C_{20}H_{28}N_2O_2$ or $C_{19}H_{24}N_2O_2$ is the correct formula for quinamine cannot be decided from the author's analyses. Many of the properties of this alkaloïd have been described by Hesse (*Ber.*, **5**, 265; *ibid.*, **10**, 2157; *Annalen*, **166**, 266; this Journal, 1878, Abstr., 436). Quinamine may be detected by the orange or chestnut colour which is produced by the action of strong sulphuric acid containing a small quantity of nitric acid. On the addition of water, the colour changes through purple to pink.

When paper moistened with a solution of quinamine in sulphuric acid is placed over a vessel in which chlorine peroxide is evolved, a brown or olive-coloured stain is produced, which turns blue on exposure to the air and becomes pink when moistened with water.

100 part of pure ether at 16° dissolve 2·06 parts of the alkaloïd. In addition to the salts which have been previously described by Hesse, the nitrate, chlorate, perchlorate, and formate were prepared. The latter forms feathery crystals, soluble in water. The *nitrate*, $C_{19}H_{24}N_2O_2.NO_3H$, crystallises in the monoclinic system. It is freely soluble in alcohol and in warm water. The specific rotatory power of the nitrate in aqueous solution (1—2 per cent.) is +116·8°, and in alcoholic solution of the same strength +131·8°. The *chlorate* forms rhombic prisms which require 137 times their weight of water for complete solution at 16°. The crystals are more soluble in alcohol. The *perchlorate* crystallises in the monoclinic system. The *platinochloride* is sparingly soluble in water, but is soluble in water containing hydrochloric acid, hence the alkaloïd is not completely precipitated from its solution on the addition of platinum chloride. The double salt slowly decomposes when left in contact with water, a pink solution being formed.

Experiments on the rotatory power of quinamine in solutions containing varying amounts of different acids show that the maximum rotatory power is nearly attained when 1 mol. of a monobasic or $\frac{1}{2}$ mol. of a bibasic acid is added to each molecule of the alkaloïd: hence the author concludes that quinamine is monacid. W. C. W.

Bidara Laut. By H. G. Greenish (*Pharm. J. Trans.* [3], **9**, 1013—1014).—Since a difference of opinion existed as to the presence of strychnine in the *Bidara laut*, careful qualitative and quantitative analyses of the wood and bark were made by the author, but although no traces of strychnine were found, the quantity of brucine amounts in the wood to 2·26 per cent. and in the bark to 7·38 per cent. The author shows that Bidara laut belongs to the natural order *Laganiaceæ* and not to either *Rhamnaceæ* or *Simarubaceæ*, as previously supposed. Owing to the absence of strychnine, the wood or bark is a good source of pure brucine. L. T. O'S.

Alkaloïd of Mio-Mio (Baccharis cordifolia). By P. N. Arata (*Pharm. J. Trans.* [3], **10**, 6).—The mio-mio occurs in Uruguay and the Brazils, and contains an alkaloïd having powerful tonic properties. The alkaloïd may be extracted by heating the dried plant several times with hot water, concentrating the solution to the consistency of a syrup, treating with a mixture of lime and magnesia, and evaporating to dryness. The dry mass is then powdered, exhausted with amyl alcohol, and filtered. On evaporation, the filtrate deposits needle-shaped crystals, soluble in amyl alcohol, in ether and in alcohol, and sparingly in water. It gives the reactions characteristic of the alkaloïds, but the aqueous solution is neutral to litmus paper. It forms an acetate which is more soluble in water than the free acid. The author proposes to call this alkaloïd *baccarine*. L. T. O'S.

Physiological Chemistry.

Existence of Bacteria or their Germs in the Healthy Organs of Animals. By M. Nencki and P. Giacosa (*J. pr. Chem.* [2], **20**, 34—44).—Chiene and Ewart (*J. of Anal. and Physiol.*, 1878, 448) find that neither Bacteria nor their germs exist in the healthy organs of animals. The authors, however, find by experimenting, first, with slices of organs of a rabbit extracted with great care under a spray of carbolic acid and dipped into a bath of molten Wood's metal (m. p. 75°) until the metal solidified round the fibre, and secondly, with the organs collected in tubes filled with mercury and placed in a bath of this metal at 120° and then allowed to stand some days at 40°, that in both instances putrefaction set in after a few days. The temperature to which the metals were heated before experiment was sufficiently high to destroy all germs, and to prevent the entrance of the latter from the air, as the baths were covered with a layer of carbolic acid solution. P. P. B.

Feeding Calves without the Cows' Milk. By E. Wein (*Bied. Centr.*, 1879, 470).—An attempt to replace the mother's milk for sucking calves by a warmed mixture containing oat and bean meal did not succeed, as the calves suffered from diarrhœa in consequence of the diet. J. K. C.

Fowls Poisoned with Pumpkin-seeds. By Hille (*Bied. Centr.*, 1879, 471).—The illness shows itself first in lameness; in many cases the birds die. No remedy is known. J. K. C.

Chemistry of Vegetable Physiology and Agriculture.

Method of Photographing Bacteria. By Koch (*Bied. Centr.*, 1879, 480).—A thin layer of liquid containing Bacteria is evaporated on a plate of glass, which is then coloured with a little aniline brown, and the photograph taken with the aid of a microscope. J. K. C.

Non-existence of a Soluble Alcoholic Ferment. By D. Cochin (*Compt. rend.*, **89**, 315—316).—If the yeast plant is cultivated in a non-fermentable medium and the liquid filtered, the filtrate will not produce alcoholic fermentation in a saccharine solution. Hence the author concludes that a soluble alcoholic ferment does not exist, and that fermentation is a direct consequence of the living yeast cells. W. C. W.

Cultivation of Pure Beer-yeast. By J. Bersch (*Bied. Centr.*, 1879, 459—462).—The author after commenting on the difficulty of obtaining a pure yeast, gives full details of a process by which a very small quantity of the pure material may be made in a short time to

yield a large amount sufficient for ordinary purposes, and comparatively free from impurity; he was, however, not able to thoroughly purify the yeast from lactic ferment, and the beer made with it contained a small quantity of acid. J. K. C.

Nitrification. By E. W. Davy (*Pharm. J. Trans.* [3], **10**, 1—3).—In order to ascertain the circumstances most favourable to the formation of nitrites and nitrates in waters contaminated with sewage, the author has carried out a series of experiments on water mixed with urine and feculent matter.

Warington (this Journal, Trans., 1878) considers that darkness is an essential condition for the development of that low form of vegetable life which is supposed in many instances to give rise to nitrification, but the author has failed to detect any difference in the quantity of nitrites formed by exposing the liquid to the action of sunlight, or by entirely excluding the light. He, however, is of opinion that the presence of air is necessary for the production of these bodies.

The quantity of organic matter in solution exerts an influence on the quantity of nitrites formed, inasmuch as when present in very large proportions it decomposes the nitrates soon after they are formed.

Temperature also exerts a very great influence over nitrification, the formation of nitrites and nitrates being very rapid between 70 and 80° F., whereas at the ordinary temperature it only takes place slowly.

The author points out the necessity of examining waters for nitrites as soon as possible after they are collected, since by keeping, nitrites are rapidly formed at the expense of the free ammonia. In one case the free ammonia decreased in a few days from 0·976 to 0·186 grain per gallon, the nitrites increasing proportionally.

The proof that the development of vegetable organisms is necessary to the formation of nitrites seems to the author to be insufficient.

L. T. O'S.

Influence of Light on the Yield of Beet-sugar. By H. Briem (*Bied. Centr.*, 1879, 473).—The author planted part of a field with willow saplings, and between these beets were sown, as well as on the open part. The beet grown in the open showed 11·14 per cent. of sugar, and 320 grams of root to 100 of leaf, whilst the beet grown amongst the willows gave 8·8 per cent. of sugar and 40·3 grams root to 100 of leaf. The effect on potatoes was similar. J. K. C.

Influence of Heat on the Ripening of Grapes. By R. Portele (*Bied. Centr.*, 1879, 472).—Levi has expressed the opinion that the amount of sunlight governs the quantity of acid in the grapes, whilst Portele thinks that the warmth of the weather has the greater influence, and adduces the following table in favour of his view:—

Year.	From March 1st to October 10.			Percentage of Free Acid in the Must.	
	Total warmth.	Fine days.	Dull days.	Teroldigo.	Negrara.
1875	2868	78	35	5·9	6·3
1876	2314	81	68	7·8	8·8
1877	2474	65	50	8·2	8·2
1878	2639	86	35	6·6	7·0

J. K. C.

Influence of Temperature on the Evolution of Carbonic Anhydride by Barley Seeds. By R. Pedersen (*Bied. Centr.*, 1879, 473).—When the seeds were allowed to sprout in the dark, the author found that the quantity of carbonic anhydride increased with the temperature between 0° and 35°, but not proportionally; at lower temperatures, it increases very slowly, and from 15—18° very rapidly; above 33·5° seems the best temperature, but even at 0°, carbonic anhydride is evolved. J. K. C.

Digestive Ferment of Carica Papaya. By A. Wurtz and E. Bouchut (*Compt. rend.*, **89**, 425).—The juice obtained by making incisions in the bark of the above tree separates spontaneously into two portions, an insoluble pulp and a limpid colourless liquid.

From the latter of these, alcohol precipitates a body, which, after suitable purification, presents the characters of a strong digestive ferment, resembling that secreted by carnivorous plants. When pure, it is an amorphous white powder, entirely soluble in water, a property which shows the absence of vegetable albumin. It contains 10·6 per cent. of nitrogen. Its aqueous solution has an astringent taste, gives an abundant precipitate with alcohol, also with nitric acid soluble in excess to a yellow liquid; acetate of lead and tannin also precipitate it from its solution.

Placed in contact with moist fibrin in slightly acid, neutral, or slightly alkaline solution, it dissolves large quantities of that substance, the fibrin first softening, then disintegrating, without swelling, and dissolving, leaving a residue of dyspeptone.

The above-mentioned pulp, even after careful washing, presented similar characters. C. W. W.

Action of the Sap of Carica Papaya. By L. Wittmak (*Bied. Centr.*, 1879, 475).—The sap of the *Carica papaya* contains a ferment analogous to pepsin, from which it is distinguished by its acting on milk quickly without addition of acid. On boiling a solution of the sap, or on adding mercuric chloride, iodine, or mineral acids, a precipitate is formed. This substance resembles pepsin in being precipitated by neutral lead acetate and silver nitrate, but not by potassium ferrocyanide or ferric chloride. 1 mgm. of the dried sap coagulated 10 c.c. of milk at 35°. J. K. C.

On the Saccharine Matter contained in Vines suffering from the Phylloxera. By GAYON and MILLARDET (*Compt. rend.*, **89**, 288—291).—The authors deny the accuracy of Boutin's statement (*Recueil des Savants Etrangers*, 25, No. 6) that the cane-sugar in the root of the vine is converted into glucose when the plant is attacked by phylloxera, but they find that the amount of sugar decreases as soon as the root begins to decay. It is highly probable that the sugar is consumed by the fungus growth which causes the root to decay. W. C. W.

Analysis of the Orange. (*Analyst*, 1879, 149).—A medium-sized Florida orange gave the following results:—

	Grams.		Per cent.
The skin weighed.....	57·5	=	23·33
„ seeds „	7·0	=	2·84
„ pulp „	182·0	=	73·83

The skin contained in 100 parts:—Water and volatile oil = 78·00; organic matter = 21·36; ash = 0·64.

The seeds contained in 100 parts:—Water = 50·00; organic matter = 48·64; ash = 1·36.

The pulp contained in 100 parts:—Water, 90·99; organic matter, 8·63; ash, 0·33.

The pulp contained in 100 parts:—Grape-sugar, 4·3; cane-sugar, 4·2; free acid, 1·0. The free acid consisted of about equal parts of malic and citric acids.

The ash contained:—

KHO.	NaHO.	CaO.	MgO.	$FePO_4$.	S.	SiO_2.	P_2O_5.
38·7	7·6	23·0	6·5	1·7	2·9	5·2	14·1

From these results it is seen that the orange does not greatly exhaust the soil; indeed it would appear that the growth of fruit depends so slightly upon important inorganic constituents, that fertilisation in good soils is hardly necessary. The food most largely drawn upon for the formation of skin, pulp, and seeds, is potash, and next come lime and phosphoric acid. In 100 lbs. of the fruit there are but $2\frac{1}{3}$ lbs. of ash, and nearly 1 lb. of this is potash. It is evident that ashes and phosphoric acid are the forms of food demanded in the growth of the orange, and on poor soils this may be supplied with advantage. D. B.

Preservation of Green Fodder in Pits. By G. LECHARTIER (*Compt. rend.*, **89**, 364—367).—The experiments made by the author show that the carbonic anhydride which is evolved when green fodder is preserved in a pit, protects the vegetable mass for a considerable time from the action of the atmosphere. The fodder is liable to be attacked by mildew as soon as the liberation of carbonic anhydride ceases.

Beetroots may be advantageously preserved in the earth, since there was no sign of fermentation in beetroots which had remained under ground during the whole of the winter. W. C. W.

Nutritive Value of Malt. By O. Kellner (*Bied. Centr.*, 1879, 417—418).—As the mean result of the analysis of five samples of malt, the author finds the total amount of nitrogen present to be 4·33 per cent., of which nearly one-third is in the form of amido-acid or acid-amide. The percentage of proteïn, he finds to be 19·5. J. K. C.

Use of Sour Food for Cows. By H. Cottu (*Bied. Centr.*, 1879, 415—417).—A variety of soured fodder, consisting of maize, mixed with young oat straw, rye, &c., was used by the author in the feeding of 15 cows. At the beginning of September, 1877, the average weight per head was 405 kilos., and at the end of the next year it had risen to 525 kilos.; the soured food appeared to be very wholesome, not one case of illness occurring during that time. The yearly yield of milk amounted to 3650 litres. J. K. C.

Spent Hops. By Kleemann (*Bied. Centr.*, 1879, 471).—An analysis of spent hops was made, in order to ascertain its value as fodder. The dried material was found to contain:—Ash, 4·9; ethereal extract, 6·16; nitrogenous substance, 16·27; nitrogen-free, 45·07; fibre, 27·60 per cent. This shows that spent hops may be advantageously used as fodder. J. K. C.

Exhaustion of the Soil by Beetroot Cultivation. By Liebscher, Briem, and R. Burger (*Bied. Centr.*, 1879, 401—407).—The failure of the beetroot crops was formerly considered to be due to the absence of potash in the soil, but the authors have shown by analysing various samples of earth from land which is suitable as well as unsuitable for the growth of beetroot, that this is not the case. A parasite, "Heterodera Schachtii," seems, however, to be the cause of the failure of the crops, as soil freed from this parasite gives a good yield of the root, whilst its presence causes a failure. The authors treat of their experiments on this point at some length, and also on the means of removing the parasite. J. K. C.

Artificial Manures. By R. Heinrich (*Bied. Centr.*, 1879, 468).—The author has analysed several so-called "gypsum manures," and finds them to consist chiefly of quicklime and carbonate, the highest percentage of gypsum in a sample being 5. J. K. C.

Experiments with Artificial Manures. By v. Massenbach (*Bied. Centr.*, 1879, 469).—Further researches (comp. p. 958) have confirmed the author's opinion that ammoniacal superphosphate should be applied in winter, especially in the case of a rye crop. The best time of the year for manuring with Chili saltpetre would seem to be the end of March, but it varies according to the nature of the soil; a rye crop is injured by using much Chili saltpetre, whereas the opposite takes place in the case of oats. J. K. C.

Experiments on Manuring. By F. Schaffert (*Bied. Centr.*, 1879, 410—412).—The author states some of the results of the experiments at Donaumoos, in 1877. The largest yield of rye and potatoes was obtained by using a manure consisting of stable dung, superphos-

phate, and cainite; and the smallest, which was about one-half the former, by using no manure at all. The largest amount of hay was yielded by manuring with Peruvian guano, and the smallest quantity, about the tenth part, was cut from land which had been left without manuring. J. K. C.

Chili Saltpetre as a Manure for Barley. By Bochmann (*Bied. Centr.*, 1879, 412—413).—The object of this research was to determine the most advantageous quantity of Chili saltpetre to be used and the best time for applying it. The author found that by treating the soil with 50 kilos. of the saltpetre per acre, the largest yield both of straw and corn was obtained one month after sowing the barley; whereas in using 25 kilos. at the time of sowing, the larger yield of seed in proportion to the straw was obtained. This the author explains by the fact that the plot which was manured with 25 kilos. of saltpetre a month after sowing was to a large extent covered with weeds. The following are the numbers which were obtained:—

		Produce. Corn.	Straw.
1.	50 kilos. Chili saltpetre applied on April 2	310 kilos.	406 kilos.
2.	25 „ „ „ „ „ 13	376 „	445 „
3.	50 „ „ „ „ „ 13	377 „	509 „
4.	50 „ „ „ „ „ 29	411 „	562 „
5.	50 „ „ „ „ May 13	534 „	692 „
6.	25 „ „ „ „ „ 13	326 „	490 „
7.	25 „ „ „ „ „ 29	321 „	438 „
8.	Unmanured.....	301 „	441 „

The seed was sown on the 13th of April. (Compare this vol., pp. 828 and 958.) J. K. C.

Analytical Chemistry.

Estimation of Iodine in Varec. By O. Schott (*Zeits. Anal. Chem.*, 1879, 443—446).—The author describes the method finally adopted by him for estimating the iodine value of samples of varec: exactness is necessary, since the percentage of iodine is usually only from 0·1 to 1·5. Bunsen's method of titration with standard sodium thiosulphate solution was found to yield precise results if the starch solution was carefully prepared and filtered, a deep blue coloration, disappearing at last on the addition of a single drop of decinormal thiosulphate solution, and reappearing on addition of a drop of iodine solution: it was therefore considered unnecessary to add excess of thiosulphate and titrate back with iodine solution. From 25 to 50 grams of dried and powdered varec were extracted with warm water several times, and the solution made up to a litre: 100 c.c. of this liquid was mixed with a few drops of sulphuric acid, and allowed to stand in a warm place for 24 hours to remove the hydrogen sulphide: the liquid, after having been evaporated to about a third its volume, was run through a small filter to remove the sulphur, and the filter was washed with as

small a quantity of water as possible. This liquid was then mixed with ferric sulphate, or ferric ammonium sulphate, and the iodine distilled over into a small quantity of potassium iodide solution contained in a **U**-tube, kept cool by immersion in cold water, the end of the delivery tube dipping several millimetres below the surface of the iodide solution. Boiling for fifteen minutes will usually distil over all the iodine, but after the residual liquid has cooled it should always be tested by carbon bisulphide or chloroform, since sometimes only long-continued boiling completely removes the iodine. The iodine contained in the potassium iodide solution is then titrated with thiosulphate. The author also tried extracting the iodides from the varec by alcohol; this method had the advantage of leaving undissolved most other salts, and especially the sulphides; the cost of the alcohol made it undesirable. A sample of varec, which yielded 0·376 per cent. of iodine by the palladium method, gave by the above process an average percentage of 0·33: and duplicate analyses of two other samples made with great care yielded 1·701 and 1·676 for the one, and 1·426 in both analyses of the other sample. F. C.

Estimation of Phosphoric Acid in Artificial Manures. (*Dingl. polyt. J.*, **232**, 363—365).—Albert and Siegfried mention that it is inadmissible to estimate the value of a superphosphate entirely by the quantity of phosphoric acid soluble in water, and that the phosphoric acid soluble in ammonium citrate should be taken into consideration.

According to Meinert, the Livonian fisheries yield annually 20 to 22 millions cod fish, the head and spine of which at present form the chief material for preparing Norwegian fish guano. Dietzell and Gressner have found that by fusion with nitre, the estimation of phosphoric acid gives higher numbers than by fusion, and that part of the phosphorus is probably present in organic combination. As this portion of the phosphorus does not possess the same manuring value as the phosphoric acid, it is recommended to dissolve the guano in acids, or ignite it previously, but not to fuse it with nitre. D. B.

Insoluble Phosphoric Acid in Superphosphate. By A. Millot (*Bied. Centr.*, **6**, 408—410).—The author makes some critical observations on the French method of estimating superphosphate by the percentage of matter soluble in citrate or oxalate of ammonia: after showing that this method fails when oxide of iron or alumina is present in any quantity, he describes the following method of his own:—The phosphoric acid soluble in water alone and in acetic acid is first determined, and next the quantity soluble in cold citrate of ammonia; when the first two results are subtracted from the third, there remains the phosphoric acid present as phosphate of iron and alumina.

As a means of obtaining all the phosphoric acid of phosphorite in the soluble condition, the author suggests mixing the phosphorite with ammonium sulphate before treatment with acid: by this means he obtained 90 per cent. of the phosphoric acid in the soluble condition, whilst without the use of this reagent only 70 per cent. was found.

J. K. C.

Volumetric Estimation of Magnesium. By H. Precht (*Zeits. Anal. Chem.*, 1879, 438—439).—To avoid the tedious method of determination of magnesium, after separation of calcium salts, by precipitation as ammonio-phosphate and convertion into pyrophosphate, the author employs for estimating magnesium in the Stassfurth salts a volumetric method depending on the insolubility of magnesium hydrate. The aqueous solution of the magnesium salt is mixed with an excess of standard potassium hydrate solution, and the excess of alkali in the solution is titrated with standard acid. The solution of 10 grams of the substance is mixed with 50 c.c. of the standard alkali if the substance contains less than 50 per cent. of magnesium sulphate, and with 100 c.c. if more than 50 per cent. is present. The potassium hydrate is of such strength that 50 c.c. of it neutralise 100 c.c. of normal sulphuric acid. The precipitation may be made in the cold, but it is hastened by heating to boiling: if the last portions of alkali solution produce no precipitate, the liquid is made up to the mark in a half litre flask, thoroughly shaken, and allowed to settle for half an hour: 50 c.c. are then drawn off clear, and titrated with decinormal sulphuric acid. By this process, magnesium sulphate crystals yielded 48·54 per cent. of $MgSO_4$ instead of 48·78 per cent.; and a sample of cainite, which by the ordinary method gave 16·50 per cent. of magnesia as magnesium pyrophosphate, yielded 16·32 per cent. The results are, therefore, about 0·3 per cent. too low, and this error is due to two causes, first, to the presence of the precipitate in the measuring flask, which causes the liquid to be too concentrated; and, secondly, some magnesium hydrate dissolves in the liquid, and is titrated as alkali. The first cause produces a minus error of 0·08 per cent. of magnesium sulphate when 50 per cent. is present, the second gives rise also to a minus error, whose amount is 0·24 per cent.; magnesium hydrate being soluble in 62,000 parts of the alkaline solution. If these errors are allowed for, the results yielded by the process are exact. The method is applicable to all soluble magnesium salts, in the absence of ammonium and metal salts: free acid is first neutralised with potassium hydrate. Calcium salts, which are precipitable by potassium hydrate, must be precipitated by neutral potassium oxalate, either before or after the magnesium hydrate: gypsum is partially decomposed by dilute potassium hydrate solution, but calcium oxalate is unaltered.

Another and less exact method depends on the solubility of magnesium chloride in alcohol and ether, in which the chlorides of the alkalis and alkaline earths are insoluble with the exception of lithium chloride. Sulphates must first be precipitated with barium chloride, calcium salts with potassium oxalate, and free acids neutralised with barium carbonate. This method is applicable to the estimation of carnallite, cainite, kieserite, and "steinsaltz" when mixed together, since the first two behave differently when treated with alcohol. Carnallite, $KCl.MgCl_2.6H_2O$, when treated with absolute alcohol, separates into soluble $MgCl_2$ and insoluble KCl: whereas no $MgCl_2$ is extracted by alcohol from cainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$: hence by volumetrically determining the magnesium chloride in solution, the quantity of potassium chloride in the carnallite can be calculated. F. C.

New Volumetric Method for Estimating Zinc. By C. Mann (*Zeits. Anal. Chem.*, 1879, 162—165).—The author proposes a new method for volumetrically estimating zinc by decomposing zinc sulphide with silver chloride, and titrating the chloride thus produced. After the zinc has been separated from other substances, it is separated from manganese by precipitation as sulphide from a solution containing free acetic acid: the excess of sulphuretted hydrogen is expelled by tumultuous boiling, until a drop of the filtrate does not alter lead test-paper: the liquid is then separated by decantation through a filter, and the precipitate, rendered much more dense by the boiling, is also thrown upon the filter and washed. The filtrate contains all the manganese. The filter and precipitate are then energetically stirred with 30—50 c.c. of hot water in a beaker, and well washed silver chloride shaken up in water is added in excess, and the mixture is boiled until the liquid above the precipitate has become clear. At last five or six drops of dilute sulphuric acid (1 : 6) are added. The zinc sulphide is thus converted entirely into chloride in a few minutes. After filtering and washing the precipitate, the chloride in the filtrate may be at once estimated, by adding silver nitrate standard solution in excess, then a few drops of ferric nitrate, and titrating the excess of silver nitrate by standard potassium sulphocyanide solution (Volhard's method). The process is rapidly carried out, an hour and a half being required from the commencement of passing sulphuretted hydrogen. The results agree well with theory and with one another. Cadmium sulphide can be similarly decomposed by silver chloride, but probably on account of the density of the sulphide, the change proceeds very slowly. F. C.

Estimation of Cobalt, Nickel, and Zinc by Precipitation as Oxalates. By A. Classen (*Zeits. Anal. Chem.*, 1879, 189—193). This method is preferable to precipitation with alkaline hydrates or carbonates, since the precipitates are more easily obtained in a pure condition, and also because it effects the separation of these metals from iron and aluminium without the trouble of precipitating the latter metals as basic acetates or salts. The precipitation and collection of the pure oxalates are carried out precisely as described in the paper on the separation of manganese from iron and aluminium (this vol., p. 1056). At a temperature of 50—60° all these oxalates become crystalline except that of nickel, and this precipitate easily separates. Free acid should be removed by evaporation on the water-bath before precipitation. The oxalates are converted into oxides by careful ignition, but the oxides must be finally heated strongly in the air to remove traces of carbon, at least in the cases of cobalt and nickel. If the oxalates have been insufficiently washed, the ignited oxides will contain potassium carbonate, which is easily recognised by litmus; it may be removed by digesting the oxides with water on the water-bath, and washing them well with hot water. Nickel and zinc may be weighed as NiO and ZnO; cobalt oxide is reduced in a stream of hydrogen and weighed in the metallic state. Results obtained by this method usually gave a deficiency of somewhat less than one per cent. for cobalt; the presence of ammonium

chloride in any quantity gives rise to a serious deficiency, potassium chloride is less injurious, and sodium acetate still less detrimental. The estimations of nickel in pure nickel solution are as satisfactory as those of cobalt; the presence of ammonium chloride and potassium chloride scarcely affects the accuracy of the results, but sodium acetate causes a deficiency. The results yielded by pure zinc solution are remarkably satisfactory, and are scarcely affected by the presence of potassium chloride or of sodium acetate, but the results are too low when ammonium chloride was present. F. C.

Separation of Manganese from Zinc. By A. Classen (*Zeits. Anal. Chem.*, 1879, 194—195).—Manganese can be entirely precipitated as carbonate from a solution containing ammonium chloride by addition of ammonium carbonate. Tamm proposes to separate manganese from zinc in this manner; but the author finds that zinc is always present in the manganese carbonate precipitate. The separation would doubtless be perfect if the manganese carbonate could be filtered off at once, but it is only completely thrown down after it has stood for some time, and during the standing some zinc carbonate is always precipitated. Quantitative experiments proved that the manganese was always too high even after reprecipitation. If the manganese only is to be determined, the author's oxalate method will serve. F. C.

New Method for separating Ferric and Aluminium Oxides from Manganese. By A. Classen (*Zeits. Anal. Chem.*, 1879, 175—189).—The author has already shortly described the principle of a method for directly precipitating manganese without first separating the iron (*Zeits. Anal. Chem.*, **16**, 471), depending on the precipitation and resolution of the manganese as oxalate by addition of neutral potassium oxalate in excess. On adding strong acetic acid to this solution, potassium manganese oxalate is decomposed with precipitation of manganese oxalate, which is completely insoluble in acetic acid. A solution of ferric salt, however, when similarly treated, yields a green solution, as the double oxalate is not decomposed by acetic acid; this difference furnishes a method for precipitating manganese in the presence of iron.

Alkaline chlorides exert an injurious influence on the precipitation of manganese oxalate; hence the method is not at once applicable to the solution of chlorides obtained by dissolving a sample of iron. But the presence of calcium oxide, or of any other metallic oxide precipitable as oxalate, is found to prevent the injurious effect of chlorides observed when manganese alone is in solution. Thus it was found that, on precipitating solution of pianoforte wire in sulphuric acid by addition of oxalic acid, the ferrous oxalate took down with it almost the whole of the manganese present, although a manganese solution containing free sulphuric acid is not precipitated at all by oxalic acid. This precipitate refused to give up its manganese when washed with water, and therefore precipitation as ferrous oxalate, and ignition of the washed precipitate, does not yield pure iron oxide. If to the manganese solution, a metal oxide is added which behaves like manganese

when treated as described above, but whose oxalate is insoluble in solutions of alkaline chlorides, the manganese is entirely precipitated as oxalate, together with the other oxalate. Zinc oxide serves this purpose, its oxalate being precipitated with quantitative accuracy by the addition of acetic acid in presence of chlorides, bromides, potassium sulphate, or sodium acetate. The zinc solution employed is made by dissolving 100 grams of pure distilled zinc in hydrochloric acid, removing excess of hydrochloric acid, and diluting to a litre. On adding this zinc solution to a liquid which contains iron and manganese oxalates and excess of potassium oxalate, and then adding sufficient acetic acid, a white bulky precipitate of zinc and manganese oxalates is formed, which contains the whole of the manganese even when the iron oxide present is one thousand times as much as the manganese oxide. This precipitate, which is bulky and would be difficult to filter when formed in a cold solution, becomes small and crystalline if the liquid is heated to 40—50°; it is filtered off, and when ignited in the air leaves a mixture of zinc oxide and Mn_2O_3, in which the Mn_2O_3 is easily determined by dissolving the ignited residue in strong hydrochloric acid, conducting the liberated chlorine into potassium iodide solution, and estimating the liberated iodine by sodium thiosulphate standard solution; two atoms of iodine correspond with one molecule of Mn_2O_3, or to two atoms of manganese. The sodium thiosulphate solution is standardised by evolving chlorine from a known weight either of potassium dichromate, or of Mn_3O_4, by treating it with excess of hydrochloric acid. For the estimation of small quantities of manganese (0·001—0·01 gram Mn_2O_3), a thiosulphate solution is employed, of which each c.c. corresponds to about 2 mgms. of Mn_2O_3, and which is made by dissolving nearly 3 grams of crystallised thiosulphate in a litre of water. For determining larger quantities (0·05—0·3 gram of Mu_2O_3), thiosulphate solutions containing 10 or 22 grams in the litre are used.

For the analysis of cast-iron not more than half a gram should be employed, and for manganiferous minerals not more than 0·9 gram; these weights suffice for the determination of the smallest quantities of manganese. The substance is dissolved in a covered beaker by means of hydrochloric acid containing bromine in solution to oxidise the iron, the beaker being heated on a water-bath until no more bromine vapour is seen above the liquid. After filtering off any gangue, the solution is evaporated to dryness, then 5—10 c.c. of bromine-water are poured over the residue, and the liquid heated for several minutes in a covered dish on the water-bath. If this oxidation is omitted, some red ferrous oxalate is liable to be ultimately precipitated together with the manganese oxalate. Solution of potassium oxalate in water (1 : 3) is added in such quantity that the weight of potassium oxalate it contains is seven times as great as that of the oxides present, including the zinc subsequently to be added. When 0·04 gram of cast-iron has been dissolved, 22 c.c. of the potassium oxalate solution will be required; the whole of the manganese and the greater part of the iron passes into solution, the undissolved iron oxide being dissolved by gradual addition of dilute acetic or hydrochloric acid with constant stirring. A green solution is obtained, which is then evaporated until the green crystals

of iron and potassium oxalate begin to separate. The solution will measure at this stage, when half a gram of iron has been employed, about 20—25 c.c. The hot solution is poured from the dish into a beaker of about 100 c.c. capacity, and the dish rinsed with hot water until the liquid measures about 40—50 c.c.; a few c.c. of alcohol are added to reduce small quantities of manganic oxide. Zinc chloride solution, prepared as already described, is then added until the zinc oxide is about four times as great in amount as the manganous oxide present. When quantities of manganese less than 1 decigram have to be determined, 4 decigrams of zinc oxide may be added, this excess of zinc being necessary to increase the bulk of the precipitate. If sufficient potassium oxalate has been added, the precipitate of zinc oxalate redissolves almost entirely as potassium zinc oxalate; potassium oxalate solution is then added until the precipitate is almost dissolved, and strong acetic acid equal in volume to the liquid to be precipitated is poured in with constant stirring. The whole liquid containing double iron and aluminium potassium oxalate in solution and the precipitate in suspension will measure about 100 c.c.; the beaker containing it is closely covered to prevent evaporation, and is heated on a sand-bath to about 60°, until the precipitate becomes crystalline and the liquid above it quite clear. Great care must be taken to avoid cooling or evaporation of the solution at this stage, as if green crystals separate, they are with difficulty redissolved, and should iron be thus introduced into the precipitate, the process of separation will have to be repeated on the precipitate after filtration. If hydrochloric acid has been added to dissolve the iron oxide, the oxalic acid thus liberated must be neutralised by gradual addition of dilute caustic alkali solution before filtration. The washings of the precipitate should measure about 350 c.c.

Results obtained as above described were always from 1 to 5 per cent. too low when about 1 decigram of manganese had to be estimated. To obtain more exact results the filtration should be carried out after the liquid has stood for about six hours. The filtration and washing should be performed as follows. The washing liquid, consisting of equal volumes of strong acetic acid, alcohol, and water, is poured on the precipitate in the beaker directly the last portion of the clear liquid has been decanted into the filter, so that the washing liquid may be poured on the filter as soon as the green liquid has completely run through. If this point is not attended to, the double iron salt crystallises in the filter-paper, and can only be removed by washing with water, which incurs loss of manganese if any of the precipitate was poured on the filter. Both precipitate and filter must be freed from the liquid containing iron by washing as rapidly as possible. The washing is complete when the washing liquid no longer gives any reaction for iron with potassium sulphocyanide. This is the case on decanting three or four times after addition of 10 c.c. of the washing liquid. The precipitate is then brought on the filter, dried, and ignited; the ignition must be commenced carefully in a covered crucible, but as soon as the oxalates have been decomposed, which is known by the residue turning dark brown, the crucible must be uncovered and heated strongly whilst in an inclined position. The

ignited residue often contains a little potassium manganate. To destroy this the contents of the crucible should be digested with hot water containing a little alcohol, then filtered, and well washed with hot water. The results obtained when due attention was paid to the above precautions were very satisfactory, yielding a maximum percentage error of 0·5, the error being usually in excess.

Instead of oxidising the iron in the hydrochloric acid solution with bromine, nitric acid may be employed. The results obtained are as satisfactory as when bromine is used. It is necessary that the metals shall not be present as sulphates, as the sulphates are not completely converted into oxalates by potassium oxalate, and the results obtained would therefore be too low. This is also the case if the residue of chlorides is dissolved by warming with dilute acetic acid.

This method effects a considerable saving of time compared with those formerly employed. It also promises to facilitate the analyses of cast-iron, from the fact that calcium, cobalt, and nickel are precipitated as oxalates, and can be determined either in a portion of the filtrate after precipitating the manganese oxalate by acetic acid, or in a portion of the original oxalate precipitate from which the zinc has been precipitated by sulphuretted hydrogen from an acetic acid solution. In estimating calcium, however, the washings of the ignited manganese and zinc oxides must be always tested with ammonium oxalate, and when cobalt is present the manganese will always be rather too high. But it is further possible to precipitate entirely as oxalates certain metals, such as copper, whose concentrated solutions are not precipitated by potassium oxalate, when metals which are entirely precipitable, such as zinc or manganese, are present in the solution. In some preliminary experiments, copper sulphate in known quantity was mixed with ferric chloride solution, zinc chloride solution was added, and the zinc and copper were precipitated as oxalates. The copper residue left after igniting the oxalates was 0·0108 gram, instead of 0·0111 gram.

Iron and aluminium may also be determined in the filtrate from the manganese oxalate. They may both be completely separated as oxalates by concentrating and adding alcohol and a little acetic acid. The precipitate becomes crystalline if the liquid is allowed to stand for a time on the sand-bath, and may then easily be filtered and washed with alcohol. By ignition, the iron and aluminium oxalates are converted into oxides, from which the accompanying potassium carbonate is easily removed by washing with water. It seems possible also to estimate phosphoric acid in the filtrate from the iron and aluminium oxalates, since it is easily precipitated from this liquid, after boiling off the alcohol and acetic acid, by the addition either of ammonium molybdate or of magnesium chloride solution; but the author has not yet proved that this process is a quantitative one or applicable in all cases. F. C.

Criticism on Bunsen's Older Method for Separating Arsenic from Antimony. By L. F. Nilson (*Zeits. Anal. Chem*, 1879, 165—175).—The method was published in the *Annalen*, **106**, 8 (1858), where it is stated that freshly precipitated arsenious sulphide is com-

pletely soluble in cold solution of potassium bisulphite mixed with sulphurous acid, and that after boiling for some time small quantities of sulphur alone remain undissolved. The salts left in solution are potassium arsenite and thiosulphate. Tin and antimony sulphides if treated in the same way are unaltered and insoluble. The method of separation consisted in dissolving the mixed sulphides in potassium sulphide solution, precipitating by addition of excess of sulphurous acid, then heating for a time on the water-bath, and finally boiling until two-thirds of the water and all the sulphurous acid have been removed. The residue of antimony sulphide is then stated to be free from arsenic, and from the filtrate, the arsenic may be precipitated at once by sulphuretted hydrogen.

In the analysis of a mineral it was found that the above filtrate, which should have contained arsenic only, contained chiefly antimony, and this led the author to make a series of experiments which proved that antimonious sulphide is permanently dissolved in considerable quantity by potassium bisulphite, unless a sufficient excess of potassium thiosulphate is formed in the solution and the filtration is deferred for some time, but the precipitate then always contains arsenic. If the quantity of thiosulphate formed in the solution is diminished by employing less potassium sulphide, some antimony invariably passes into solution. In making the above experiments, the author had used potassium sulphydrate, which was objected to by Bunsen on the ground that it must neutralise less sulphurous acid than potassium sulphide would, and yield also a larger amount of sulphur to envelop the precipitate. The author accordingly repeated his experiments, substituting potassium sulphide for the sulphydrate, and found that by treating a mixture of known weights of antimonious and arsenious sulphides by Bunsen's method, the weight of residual antimonious sulphide obtained was greater than that employed, and that it invariably contained arsenic. The presence of arsenic was proved by evaporating the residual sulphide with strong nitric acid, and testing the residue by the Fresenius-Babo method, and also by obtaining an abundant precipitate of magnesium-ammonium arsenate after fusion with sodium nitrate and carbonate. Further experiments proved that arsenious sulphide, when dissolved in solution of potassium bisulphide, and reprecipitated by excess of sulphurous acid, is by no means completely redissolved by boiling, as much as 71 per cent. remaining undissolved in one experiment. Arsenious sulphide was, however, completely soluble in solution of potassium bisulphite and sulphurous acid. Hence it seems probable that in the method as given by Bunsen, two processes, each of which is perfect in itself, are made imperfect and useless as a means of separation by being mingled. Antimonious sulphide remains quite undissolved in the presence of the large quantity of thiosulphate formed by boiling its solution in potassium sulphide, after adding excess of sulphurous acid, but the thiosulphate precipitates a large quantity of arsenious sulphide. If the proportion of thiosulphate is lessened, so as to insure complete solution of the arsenic, then antimony is also dissolved; hence the author concludes that it is impossible to separate antimony and arsenic upon the principle involved in Bunsen's method.

F. C.

Results of the Norwegian Expedition to the North Sea. By H. Tornöe (*J. pr. Chem.* [2], **19**, 401—433, and **20**, 44—76).—1. *On the Air contained in Sea-water.*—Frémy was the first to investigate the amount of gas in sea-water. As his method was to absorb the carbonic anhydride by potash, and oxygen by phosphorus, no dependence can be placed on his results. Moren, Lœwy, Hayes, and Pisani, also experimented on the subject, without, however, materially increasing our knowledge. The next memoir relating to this is one by W. L. Carpenter, Hunter, and P. H. Carpenter, who accompanied the expedition on board the "Porcupine" in 1869. Their results vary so much, that no dependence can be placed on them. They themselves ascribe their want of success to imperfections in the vessel for collecting the samples of water. In 1871 a German Expedition was sent to the German Ocean, O. Jacobsen being the chemist. Instead of performing his analyses on board ship, as was done by the English chemists, he merely collected samples of the gases given off on boiling the sea-water from different localities and depths, reserving determinations of their constituents until the expedition returned. By means of a very ingenious arrangement, the water was boiled in a vacuum, and the gases driven into a small tube, which was then sealed at both ends. The apparatus for collecting the water was designed by H. A. Meyer, and is described in the *Jahresb. der Commission*, 1872.

From his analyses of 73 samples, it appears that the amount of oxygen from surface-water remains remarkably constant, varying only between 34·14 per cent. and 33·64 per cent. Even in the lower strata, the oxygen does not fluctuate. This is accounted for by supposing that the excess of oxygen which would presumably exist in deep water on account of increased pressure, is consumed by organisms or in oxidation. The absolute amount of air increases with the depth: this is sufficiently accounted for by the lower temperature, without reference to the increased pressure. That air escaped from the water as the vessel containing it was raised to the surface was distinctly disproved by means of an apparatus contrived for the purpose. The general conclusion, therefore, is that the amount of air in sea-water remains remarkably constant, and does not materially depend on the depth from which the sample of water has been drawn.

J. Y. Buchanan, who accompanied the "Challenger" Expedition, used Jacobsen's apparatus and methods. From his published results, it appears that the absolute amount of oxygen in water decreases from the surface to a depth of 300 fathoms, and then increases.

The author used Wille's apparatus for collecting samples of water; it consists of a spiral tube with a valve at each end, which closes when the rope to which it is attached is pulled. He collected and analysed about 80 samples of air from water at various depths. His method was that of Frankland and Ward; the carbonic anhydride was removed by potash, and the oxygen by explosion with excess of hydrogen.

The chief fact to be noticed is, that the amount of oxygen in the surface-water of the North Sea is on the average 33·93 per cent. of the total air; south of latitude 70°, 34·96 per cent., and between lati-

tudes 70° and 80°, 35·64. This corresponds exactly with what Buchanan observed in the southern hemisphere.

In order to discover the connection, if any, subsisting between the amount of air dissolved in the water, and the temperature, the author ascertained the absorptive power of sea-water for air by direct experiment. His numbers are as follows. The gas is expressed in cubic centimetres per litre :—

C.	0°.	5°.	10°.	15°.
O	7·77	6·93	6·29	5·70
N	14·41	13·22	12·08	11·01
O + N = 100 O per cent.	35·03	34·39	34·24	34·11

From this table, it is seen that the nitrogen dissolved bears a very simple relation to the temperature, expressible by the formula $N = 14{\cdot}4 - 0{\cdot}23t$. The absorbed oxygen requires the more complex equation, $O = 7{\cdot}79 - 0{\cdot}2t + 0{\cdot}005t^2$. The results differ therefore from those found by Bunsen for distilled water, the absorptive power of which is independent of the temperature. But as the amount of oxygen found in sea-water usually exceeds that limit, it must be dependent not merely on pressure and temperature, but on some other causes. As a general rule, it was observed that the amount of oxygen in the surface-water averaged 35·3 per cent. of the total gas, and gradually decreased with increasing depth until at 300 fathoms it averaged 32·5 per cent.; at still greater depths, it remained nearly constant. The amount of nitrogen, on the other hand, is in accordance with the formula previously given, and is quite independent of pressure, depending on temperature alone. It therefore represents the state of the water, as regards temperature, corresponding to the last time it was at the surface, and any equalisation of the amount of air contained in the water is brought about only by mixture. By ascertaining the amount of nitrogen in sea-water, a rough indication is therefore given of any change of temperature the sea-water may have undergone since it was last at the surface. These facts are supported by several series of observations.

On the Carbonic Anhydride in Sea-water.—The old method of estimating carbonic anhydride in sea-water was to expel the gas by boiling the water, and estimate it by the usual processes. The results obtained, however, were not concordant. Jacobsen ascribes his irregular results to the attraction of a solution of salts in water for carbonic anhydride, in opposition to Vierthaler's view, that the carbonic anhydride as it exists in sea-water is in combination with bases.

The author was led to investigate the latter theory by an accidental observation that sea-water is faintly alkaline to test-paper. His first experiment had for its object to ascertain whether the salts contained in sea-water have the power of expelling carbonic anhydride from carbonates. This was proved to be the case, and by long-continued boiling, a large amount of carbonic anhydride may be collected. For the purpose of determination, he therefore made use of Alex. Classen's apparatus, of which a description is given in the *Zeits. Anal. Chem.*, **15**, 288. The principle is to expel the gas by boiling with dilute

sulphuric acid, and absorb it with normal baryta-water, the excess of baryta being determined with standard oxalic acid, and the excess of sulphuric acid by standard soda solution. The carbonic acid existing in neutral and acid combination was thus determined.

From 78 observations of the amount of carbonic anhydride in sea-water from every depth, and many different places, nothing can be inferred as to the laws of its distribution. All that can be done is to take the mean of all the determinations. One litre of sea-water contains on the average 52·78 mgms. of carbonic anhydride in neutral, and 43·64 mgms. in acid combination.

The reason of the gradual and complete expulsion of all the carbonic anhydride by continued boiling is to be sought for in the presence of magnesium chloride, which, as the author has experimentally proved, decomposes into hydrochloric acid and magnesia, when boiled for a long time even in dilute solution. On evaporating sea-water, therefore, no trace of carbonates is to be found in the residue, since the carbonic anhydride is all expelled by the action of the magnesium chloride. W. R.

Sugar as a Test of the Purity of Water. By J. E. Reynolds (*Bied. Centr.*, 1879, 467).—Half a litre of the water to be tested is introduced into a flask, and a piece of white sugar about the size of a pea put in: the mouth of the flask is covered with paper, and the flask left in the sunlight for eight or ten days. The presence of much organic matter in the water will cause it to become muddy.

J. K. C.

Estimation of Nitrates in very Dilute Solutions. By A. Leeds (*Zeits. Anal. Chem.*, 1879, 428—430).—The author finds that in apparatus for detecting or estimating small quantities of ammonia or nitrates, by distilling and determining colorimetrically by Nessler solution the amount of ammonia in the distillate must be free from india-rubber stoppers and joints.

It was found that continuous distillation of water free from ammonia always yielded distillates containing ammonia, and the quantity of ammonia found was always larger if the coppered zinc used as a reducing agent for nitrates was present in the water undergoing distillation. After distilling 50 c.c. of ammonia-free water three times from such an apparatus, subsequent distillates of 50 c.c. repeated eight times in succession yielded ammonia varying from 0·05 to 0·01 mgm. when the coppered zinc was present, and from 0·03 to 0·01 mgm. when cast-iron was present, the quantity increasing the more nearly the liquid was distilled to dryness. The author avoids the necessity of joints, by distilling out of a tubulated retort with glass stopper, whose neck dips as deeply as possible into the vessel in which the estimation is to be made, and which is kept cold by standing in cold water. The distillates from such a vessel gave quantities of ammonia which were not increased by the presence of the copper-zinc or cast-iron; after three times distilling pure water from the retort, the fourth distillate usually contained 0·01 mgm. of ammonia, and the fifth an average of 0·004 mgm., which in the sixth was reduced to 0·0025 mgm. Hence it is evident that even when india-rubber corks and joints are

absent, it is necessary, before introducing the substance to be tested, to distil water to which the reducing metal has been added until the distillates are free from ammonia. In one case as much as 0·0175 mgm. of ammonia was thus obtained from well-washed coppered zinc, owing doubtless to nitrogen-compounds it had taken from the air whilst being transferred to the retort. This affords an explanation of the facts that small quantities of ammonia have been obtained by distilling cast-iron with sodium hydrate solution, and that when small quantities of alkaline nitrates are estimated by distillation with excess of cast-iron a slight excess of ammonia is obtained. It was established by experiment, however, that with the above precautions the distillation of 50 c.c. of water containing 0·0061 gram of potassium nitrate with 6 grams of cast-iron yielded almost precisely the theoretical quantity of ammonia. Hence cast-iron alone serves as a sufficient reducing agent when the quantity of nitrates present is small, as in drinking waters, and when the proportion of cast-iron employed is in large excess. In the above experiment the proportion of iron to nitrate was 1000 : 8; a trial with about 15 times as much iron as nitrate yielded less than 5 per cent. of the nitrate present. F. C.

Petroleum Spirit and Benzene. By A. H. Allen (*Chem. News*, **40**, 101).—Although presenting close general resemblances, many characteristic differences exist between petroleum spirit and benzene. The author gives 10 comparative tests for petroleum spirit, benzoline, or benzine, and for coal-tar naphtha or benzene (known commercially as *benzol*), the last one being as follows :—

When petroleum is warmed with four measures of nitric acid of 1·45 sp. gr., the acid is coloured brown, but the spirit is little acted on and forms an upper layer.	Coal-tar naphtha, which consists chiefly of benzene, is completely miscible with 4 measures of nitric acid (1·45 sp. gr.), with great rise of temperature and production of dark brown colour. A portion of the nitrobenzene produced may separate as the liquid cools.

The greater number of the tests given, however, are valueless when applied to mixtures of petroleum and coal-tar naphtha, but the nitric acid test above mentioned is capable of giving quantitative results if the treatment with nitric acid be conducted in a small flask and an inverted condenser attached to prevent loss of vapours. When the action has nearly ceased, if the liquid be poured into a narrow graduated tube, the measure of the upper layer indicates with approximate accuracy the amount of petroleum spirit present. D. B.

Limit of Detection of Carbonic Oxide. By W. Hempel (*Zeits. Anal. Chem.*, 1879, 399—403).—The detection of carbonic oxide in the air heated by stoves is important for sanitary reasons. Of the processes employed for this purpose, Vogel's deserves the preference over those by palladium sodium chloride, and cuprous chloride, since its indication is quite decisive even in presence of hydrocarbons and of oxygen. Vogel introduces into a flask of 100 c.c. capacity, which has been

filled with the gas to be tested, 2 or 3 c.c. of water, containing sufficient blood to have a reddish tint, and to show in a test-tube the characteristic absorption-bands. The flask is well shaken for a few minutes, when if carbonic oxide is present, a change to rose colour is noticed, and addition of colourless ammonium sulphide does not cause the absorption-bands to disappear or to change into an indistinct broad band, as is the case when the sulphide is added to blood free from carbonic oxide. Vogel found that 0·25 per cent. of carbonic oxide could be detected by this process, and that the employment of larger quantities of air did not augment its delicacy. The author's experiments proved that a small proportion of carbonic oxide could not be completely absorbed by such dilute blood solutions, and undiluted blood or stronger solutions frothed so much when shaken as to be inapplicable. He tried, therefore, exposing the gas to undiluted blood by making a mouse inhale it for some time, and then obtaining a sample of the blood from its heart immediately after it had been killed. A mouse was inclosed between two glass funnels fitted mouth to mouth, the joint being made gas tight by sheet india-rubber; air mixed with known proportions of carbonic oxide was drawn through the funnels, and after the experiment was finished, the mouse was drowned by plunging the funnels into water. The gas was passed at the rate of 10 litres in one or two hours, and this prevented poisoning by carbonic anhydride produced by respiration. Vogel's method was compared by passing the air, before or after its passage through the funnels, through the dilute blood solution contained in Liebig's potash-bulbs. In every case blood free from carbonic oxide and of the same dilution was compared with the sample after addition of colourless ammonium sulphide; the difference of colour was then evident, the solution which contained carbonic oxide remaining more reddish in colour.

The author's experiments proved that when large quantities of gas (at least 10 litres) were employed, Vogel's method readily detected 0·05 per cent. of carbonic oxide; and that when the blood was taken from a mouse which had inhaled the gas 0·05 per cent. was the least proportion which could be recognised.

Symptoms of poisoning became evident in half-an-hour when 0·05 per cent. of carbonic oxide was present, and when the proportion reached 2·9 per cent. the mouse died in about two minutes; hence the presence of even minute traces of carbonic oxide in air is to be avoided. The author suggests the plan of confining the mouse under a wire-net cover in the air. F. C.

Decomposition of Mercuric Cyanide by Dilute Acids alone and in presence of Sodium Chloride. By P. Plugge (*Zeits. Anal. Chem.*, 1879, 408—417).—The strong affinity which exists between mercury and cyanogen is shown by the development of heat on dissolving mercuric oxide in hydrocyanic acid even when dilute, and also by the action of hydrocyanic acid on mercury salts forming the cyanide of the metal with liberation of the free acid of the salt; further mercuric oxide acts on alkaline cyanides, forming mercuric cyanide, and mercuric cyanide in solution yields no precipitates with

potassium or ammonium hydrate, with potassium iodide, or silver nitrate. It has been inferred from these facts that mercuric cyanide withstands decomposition by other acids to a remarkable degree.

Berthelot's thermo-chemical experiments proved that in dilute solutions hydrocyanic acid completely converts mercuric chloride into cyanide; gaseous hydrochloric acid, however, completely changed dry mercuric cyanide into chloride: hence it was assumed that strong liquid hydrochloric acid liberated hydrocyanic acid from mercuric cyanide, because the hydrate was accompanied with anhydrous hydrochloric acid. Toxicological text-books generally assume that the organic acids in the food and stomach cannot liberate hydrocyanic acid from mercuric cyanide, and that the acid cannot be separated and detected by distillation with hydrochloric acid if mercuric cyanide is present. The author's experiments, made by distilling mercuric cyanide with dilute acids present in four times the quantity theoretically sufficient to liberate the hydrocyanic acid, proved that hydrochloric acid can thus set free four-fifths of the acid, oxalic acid about one-twentieth, and tartaric and sulphuric acids about one-fiftieth. From this it appears that hydrochloric acid is best suited for liberating hydrocyanic acid from mercuric cyanide with a view to its detection; but as hydrochloric acid renders the substance unsuited for further researches, the author prefers distilling with oxalic acid and sodium chloride, which can liberate by distillation nearly 50 per cent. of the hydrocyanic acid producible from the mercuric cyanide.

In order to ascertain the delicacy of this method, experiments were made on a solution of mercuric cyanide containing 10 mgms. in 1 c.c., equivalent to 2·128 mgms. of hydrocyanic acid, and it was found that a liquid containing a quantity of mercuric cyanide equivalent to one twenty-five-thousandth of hydrocyanic acid, yields by the above process unmistakeable evidence of the presence of the acid. Many foods and contents of the stomach which contain sodium chloride will yield hydrocyanic acid on distillation after the addition of oxalic acid only.

F. C.

The Ebullioscope. By P. Waage (*Zeits. Anal. Chem.*, 1879, 417—428).—The author publishes the results of experiments made to ascertain the value of this instrument for determining the percentage of alcohol in beer. The first series of results were those obtained from mixtures of pure spirit and water, and were designed to ascertain whether the adjustment of the zero of the scale to the boiling point of water at the barometric pressure observed at the time of experiment was a sufficient correction for variations of atmospheric pressure; and also whether the indications of the instrument are equally reliable for low and high percentages of alcohol. The adjustment for barometric pressure was proved to yield a correct result; but the scale of the instrument employed was not correctly graduated, as it showed an error increasing with the proportion of alcohol present, and reaching 0·1 per cent. with 20 per cent. by volume of alcohol; this error, however, was only about 0·01 per cent. for ordinary beer, and was therefore insignificant in the present inquiry. Two marks are made on the instrument, the one to indicate the height to which pure water is poured in for the determination of the zero, the other shows

how much of the alcoholic liquid is required. The volume of water required is apparently without influence, as is also the volume of weak alcohol solutions; but when about 16 per cent. of alcohol is present, attention must be paid to the volume of liquid employed.

A second series of experiments was made by mixing with pure water known proportions of one or both of the following liquids, absolute alcohol and a strong solution of extractive matter obtained by evaporating five bottles of Bavarian beer to about 750 c.c., and making this up to 1 litre. The object of these experiments was to ascertain the influence of extractive matter on the accuracy of the results yielded by the ebullioscope. The presence of extractive matter in pure water exerted no influence in the determination of the zero point of the scale. When, however, both alcohol and extractive matter were mixed with water, the result obtained was too high, and the error was increased by increasing the proportion either of alcohol or of extractive matter; the alcohol, however, appeared to exert the greater influence. These experiments do not pretend to great accuracy, but only indicate the nature of the error involved. This error is easily corrected in the case of beer, since the alcohol and extractive matter will vary similarly in amount, and hence it is easy to find what correction must be applied for any percentage of alcohol indicated.

Experiments were made to ascertain what correction must be applied, by determining in a number of samples of Bavarian beer: (1) the percentage of alcohol directly by the ebullioscope; (2) the percentage indicated by the ebullioscope in the distillate from a measured quantity of beer made up to the original volume; (3) the percentage indicated in the same liquid by the sp. gr. The results yielded by (2) and (3) agreed closely. But it was found that if over 6 per cent. by volume of alcohol is indicated by (1), 0·216 per cent. must be deducted, leaving a possible error of 0·035 per cent. in each estimation. If method (1) shows from 5 to 6 per cent. by volume of alcohol, 0·159 per cent. must be deducted, leaving a possible error of 0·028 per cent.; and as a result of a few experiments made with beer prepared by surface fermentation, the error of excess for 4 to 5 per cent. of alcohol is 0·11 per cent., and for 2 to 4 per cent. of alcohol the error is 0·02 per cent. By applying the above corrections then, the possible error of the alcohol estimation in a beer by the ebullioscope will never reach 0·1 per cent. Experiments were further made to determine the cause of the above error; they seemed to prove that the ebullioscope indicates not the percentage of alcohol in the beer, but the percentage which would exist if all the solid constituents were removed from the beer.

The author concludes with offering various suggestions as to improvements in the construction and use of the instrument, to increase the accuracy of its indications and convenience in its manipulation.

F. C.

The Ammoniacal Copper Test and its Application. By J. Steiner (*Chem. News*, **40**, 139).—The author has investigated this process in order to determine whether it could be applied with advantage to the estimation of sugar in malt liquors, especially when old, black, or "turning" beers are to be analysed. In these instances

the volumetric determination with Fehling's solution does not give very satisfactory results, in consequence of the appearance of a deep straw-yellow colour after boiling for some time, and when about three-fourths of the total cupric oxide has been reduced. The same is the case when the amount of glucose or "uncrystallisable sugar" in jaggery, China, or Jamaica sugars has to be ascertained, and in other instances, especially with old pale ale or old lager beer, where the sugar in the beer is reduced by after-fermentation to less than one-half per cent. Unless the beer solution is added gradually to the copper test and the boiling is repeated several times, a muddy hydrated copper suboxide is separated and remains suspended in the liquor, in which case even filtering is useless and the test has to be put aside. The author has devised an apparatus by means of which he is able to apply the ammoniacal alkaline copper test. The results obtained for such cases as the above are, however, only approximate, and it is therefore necessary to resort to the application of the polariscope, which, considering the large amount of substance used for a "normal solution," offers much more trustworthy data for calculation, and its indication should therefore never be neglected in the analysis of starch-sugar. The author nevertheless considers the ammoniacal copper test as most valuable for telling by merely analytical means whether a starch-sugar or a beer contains only one sugar, or if two of them are present; and such analysis may be safely relied on if there be only one sugar, as in diabetic urine, or in most beers and in raw sugars.

D. B.

Estimation of Urea in Urine. By G. Esbach (*Compt. rend.*, **89**, 417).—The author concludes from his experiments that in a mixture of glucose and urea, the gas evolved by treatment with sodium hypobromite varies with the proportion of glucose present. Sodium hypobromite causes the evolution of large quantities of gas from glucose solutions. The quantity of gas evolved from urea is increased by the addition of glucose.

C. W. W.

New Test for Papaverine. By J. Tattersall (*Chem. News*, **40**, 126).—Papaverine, when brought in contact with concentrated sulphuric acid, gives a light pink-violet colour. On heating, this either disappears completely or becomes a light grey, but the following reaction is more permanent and more characteristic of the alkaloïd:—Place the substance to be tested in an evaporating basin and heat with concentrated sulphuric acid and a fragment of sodium arsenate. A dark bluish-violet colour is finally obtained, which is very stable. When the contents of the dish are cold, add 10 c.c. of water and pour the orange liquid obtained into a flask, dilute once more and add soda to strongly alkaline reaction; the liquid rapidly darkens in colour, and when an excess has been added appears almost black; it is violet-red by reflected, and a pink-straw colour by transmitted light. Strychnine, brucine, morphine, salicin, atropine, narcotine, narceine, digitaline, picrotoxin, curarine, colchin, and cantharidin do not exhibit this reaction, becoming, on subsequent addition of alkali, light orange or dirty yellow.

Codeine, when heated with sulphuric acid and sodium arsenate

gives a fine deep blue colour, much darker than the one produced by ferric chloride under similar circumstances. On addition of water and alkali this becomes orange, and is characteristic of the alkaloïd.

D. B.

Detection of Milk Adulteration. By W. H. Watson (*Chem. News*, **40**, 102).—From analyses of milk from various dairies and by a comparison of the results obtained with the circumstances existing as to the character and quantity of the food, nature of different cows, their condition and health at particular periods, and changes of the seasons of the year, the author concludes that cows' milk is subject to considerable variations in composition. He has found in many instances milk from well-fed healthy cows to contain as little as 10·5 per cent. of total solids and from 8·5 to 9 per cent. of solids not fat. The results of other experimenters are compared, and it is suggested that the present limits adopted by public analysts for genuine milk should be reconsidered. D. B.

Quantitative Estimation of Milk Fat. By F. Soxhlet (*Dingl. polyt. J.*, **232**, 461—465).—For determining the fat in milk, the author recommends the method of extraction by means of ether with the following modification, whereby the time is considerably reduced without interfering with the accuracy of the results. The process depends on the application of anhydrous gypsum for drying the milk and on the use of a peculiarly constructed extraction apparatus. By mixing the milk with burnt gypsum (20 grams for 10 c.c. of milk), the evaporation is greatly facilitated. The apparatus used for extracting the fat from the dried product is self-acting, and is constructed on the principle of washing precipitates on filters, and is described in detail in the original paper. A substance may be extracted 300 times with boiling ether in eleven hours with this apparatus; during that time, if each washing measures 25 to 30 c.c., 7·5 to 9 litres of boiling ether pass through the substance, although about 80 c.c. only of ether are required to work the apparatus. D. B.

Composition of Devonshire Cream. By A. W. Blyth (*Analyst*, 1879, 141).—The following is the average composition of Devonshire cream:—

Water.	Caseïn.	Albumin.	Galactin.	Lactochrome.
28·675	3·530	·521	·050	undetermined

Milk sugar.	Milk fat.	Ash.	Cl in ash.	Calcium phosphate.
1·723	65·011	·490	·013	·373

The analysis of Devonshire cream presents but little difficulty. A weighed portion is taken, the fat melted, and after about half an hour's exposure to the heat of a water-bath most of the caseïn, &c., settles to the bottom and the fat can be poured off as easily as that from butter. The residue remaining is now treated with petroleum and thoroughly exhausted. "The fat" and "solids not fat" are dried

separately, which is the only way in which the water can with any convenience be estimated. D. B.

New Method for Detecting Foreign Fats in Butter. By J. Koettstorfer (*Zeits. Anal. Chem.*, 1879, 431—437).—The author continues and concludes a paper the first portion of which appeared in the *Zeitschrift* for 1879, p. 199.

Further analytical results obtained by the author's method are here published, and they have led him to consider 233 instead of 232·4 as the highest number yielded by pure butter, the lower limit, 221·5, remaining unaltered. Two analyses can be completed in less than an hour, and the process has yielded concordant results in the hands of an assistant. The alcoholic potash solution is best prepared in small quantity only, as it is altered by oxidation; in making it, 32 grams of ordinary caustic potash are dissolved in 1 litre of 94 per cent. alcohol; 25 c.c. of this solution will correspond to about 18 c.c. of deminormal hydrochloric acid. The effect of a sample of butter becoming rancid is to reduce the quantity of potash solution required by 1 gram of the butter by about 1·5 mgm., since some of the acid has volatilised; rancidity does not, however, interfere with the application of the method to detect adulteration. Some samples analysed yielded the number 192·5; they probably contained no butter, and were mixtures of refined salt and oil. One remarkable specimen consisted mainly of oil, in which solid pieces of fat were floating; the oil gave the number 225, the fat 221·8; hence both portions must have come from genuine butter; when melted together in the proportions received by the retail dealer, they yielded only an oily mass. This may have been due to the butter fat having been melted by the maker, and having separated on cooling to 17° into oily and crystalline portions, as was noticed by Chevreul, the retail dealer having then received an undue proportion of the oily portion; this sample was most remarkably rancid. In comparing the above method with that of Hehner, the author considers that its trustworthiness, and the ease and rapidity of its execution, give it the preference; but in calculating the percentage of adulteration, the author has taken the average number for lard, suet, and oleomargarin, which number is too high if the adulterant is olive or other oil. Hehner's method is better suited to detect the amount of adulteration, since almost all adulterants give the same proportion of insoluble fatty acids, and it will also detect small quantities of butter in large proportions of foreign fat and oil, but for the detection of all large adulterations, the author's method is adapted. The value of a butter depends not only on its containing genuine butter-fat, but also on its comparative freedom from rancidity. An adulterated butter free from rancidity is often preferred to a genuine one whose rancidity is noticeable. The author has determined the amount of rancidity in different samples by titrating the free acid; from 3 to 10 grams of the butter, which had been repeatedly melted and filtered, was weighed into a flask of about 50 c.c. capacity; ether, freed from acidity by adding phenol-phthaleïn and then alcoholic potash until the violet colour was just permanent, was added in quantity sufficient to dissolve the butter, and the acid was titrated with alcoholic potash. The number of cubic

centimeters of normal alkali required for the neutralisation of 100 grams of butter was on an average 4, but varied in different samples from 1 to 8, and in exceptional cases to 15, 26, and even 41·6. Samples requiring 8 c.c. represented the limit which would be tolerated in good butter. F. C.

Analysis of Butter Fat. By F. P. Perkins (*Analyst*, 1879, 142).—The following method is proposed, and said to give accurate results:—Weigh out 1 to 2 grams of purified butter fat; saponify in a beaker in the usual way; drive off the alcohol; cool; set free the acids by the addition of oxalic acid; pass through a small filter; wash thoroughly, first by decantation with cold, and lastly with hot water on the filter; make up the filtrate to, say 200 c.c.; transfer 100 c.c. to a small retort with condenser, and distil slowly until the whole has passed over; add a few drops of litmus solution; titrate with decinormal potash; calculate the amount consumed by the volatile acids in 100 grams of fat; and translate to butyric acid, $C_4H_8O_2$. The insoluble acids on the filter are treated with hot alcohol, the liquid holding the acids in solution being received in a flask. The filtrate is washed with alcohol, until it no longer reddens litmus, and the filtrate is made up to 100 c.c. with alcohol. Half of this is taken, coloured with a suitable indicator, and heated gently; decinormal potash solution is run in, and the number of cubic centimeters required for neutralisation noted; the second portion is similarly treated. The first experiment serves as a guide to colour, &c.; the number of cubic centimeters used is ascertained, and the amount required by the non-volatile acids in 100 grams of fat calculated. For the purpose of comparison with fats used as adulterants, it may, perhaps, be convenient to convert this to stearic acid, $C_{18}H_{36}O_2$. D. B.

Technical Chemistry.

Heating Steam Boilers. By F. Fischer (*Dingl. polyt. J.*, **232**, 237—242, and 336—348).—In the first portion of his paper, the author gives a brief description of the results obtained by various chemists relative to the mode of ascertaining the amount of steam produced by means of a given quantity of fuel. The results obtained by Ormesson, Garnier, Johnson, de la Beche, Playfair, and Brix, are but of limited value, as they disregarded the loss of heat occasioned by the flue gases, and on this account the author considers Hartig's results more trustworthy, who found that 42 to 71 per cent. of the heating power of coal was available for the formation of steam; from these, and the results obtained by other chemists, it is assumed that practically the heating value of coal is equal to two-thirds of that calculated from its composition.

In conducting heating trials with boilers, the problem to be solved is, how much water can be vaporised with 1 kilo. of combustible.

The quantity of water to be heated is ascertained by weight or measure, but the difference between this and what is left in the boiler does not represent the actual quantity of water converted into steam, as the latter often carries with it large quantities of water (as much as 20 per cent.). Hallauer and Hugentobler determine the latter by the heat which is liberated by the condensation of a certain quantity of the steam. This method was originally proposed by Hirn, and has been since improved by Linde.

According to Knight and Guzzi, a copper vessel is filled with the steam to be examined, and the amount of water determined by weighing. It is, however, better to condense a certain quantity of the steam, and to determine in the water the chlorine, the sulphuric acid, or any other constituent which is present in the feed water, whereby the proportion of steam and water may be obtained by a simple calculation.

The quantity of combustible used is determined by weight. It is essential to conduct the heating trial for some time, as it is a difficult matter to determine whether boiler and brickwork have exactly the same temperature after the trials as before. It is of little importance to determine the heating power of the combustible for a steam boiler in its present state and under its existing circumstances, since the latter alter materially every day. It is, however, important and necessary to ascertain how much of the heat produced by the fuel is not used for the formation of steam and the causes of this loss. Such sources of error are (1) imperfect combustion; (2) the heat which is removed from the fire-grate with the ashes; (3) the heat which escapes through the chimney, in consequence of the higher temperature of the flue gases; (4) transmission and radiation. Unless the requisite amount of oxygen is admitted to boiler fires to complete the combustion of the fuel, or if the gases evolved are allowed to cool below the temperature of ignition, previous to their combination with the oxygen of the air, soot is deposited, and the flue gases will contain carbonic oxide. Although the loss of heat sustained by the formation of soot is very slight (1 per cent.), carbonic oxide gives rise to considerable losses. Thompson mentions that in the case of 42 boilers examined, 42 per cent. of the total heating value was lost by the formation of carbonic oxide, and 12 per cent. by transmission and radiation.

In the second part of the paper, Fischer deals principally with the effects produced by the flue gases. In order to determine the quantity of the latter, the air which enters the fire-place is measured by means of an anemometer. Besides the impossibility of measuring the air accurately, the results are not trustworthy, owing to the difficulty of rendering the brickwork perfectly air-tight.

Linde calculates from the quantity of heat, W_1, transmitted from a large boiler to the feed water, from the heat evolved in the heater, W_2, and from the temperature of the flue gases t_2 between boiler and heater, and t_3 behind the heater, both the total quantity of flue gases L, and the temperature in the fire-place t, by the equation

$$\frac{W_1}{W_2} = \frac{t_1 - t_2}{t_2 - t_3},$$

and $W_2 = Lc\,(t_2 - t_3)$, c denoting the specific heat — therefore

$$L = \frac{W_2}{c(t_2 - t_3)}.$$

The author mentions that although heating trials have been carried out hitherto with great accuracy as regards the temperature of the feed-water, the height of the barometer, &c., incorrect values have been taken for the specific heat of the gases produced by combustion. The following table gives the correct specific heat of the gases:—

	Air.	Oxygen.	Nitrogen.
Temperature	0—200°	10—200°	0—200°
Specific heat	0·23751	0·21751	0·2438
	Hydrogen.	CO_2.	CO_2.
Temperature	10—200°	−30—+ 10°	10—100°
Specific heat	3·4090	0·18427	0·20246
	CO_2.	CO.	CH_4.
Temperature	10—210°	10—200°	10—200°
Specific heat	0·21692	0·2450	0·59295
	C_2H_4.	SO_2.	H_2O.
Temperature	10—200°	10—200°	10—200°
Specific heat	0·4040	0·15531	0·48051

In conclusion various formulæ are given for calculating the heating effects produced by the removal of the flue gases. D. B.

Ferric Chloride as a Purifier of Water. By Gunning (*Bied. Centr.*, 1879, 467).—This has been tried with great success by the author on the water of the Maas, the quantity used being 0·032 gram per litre. After standing 36 hours the water becomes clear, and can be used without any injurious effect. J. K. C.

Preservation of Drinkable Water. By H. Schiff (*Bied. Centr.*, 1879, 466).—Experiments were made on a water which contained considerable quantities of gypsum and organic matter, and was consequently liable to become putrid in hot weather, with evolution of hydrogen sulphide. The addition of 0·3 per cent. of salicylic acid entirely prevented this, and kept the water in good condition. Carbon bisulphide and phenol are mentioned by the author as preservatives of zoological preparations. J. K. C.

Composition of a Well-water at Grouville, Jersey. By T. M. Morgan (*Chem. News*, **40**, 97).—The Female Orphans' Home of Grouville, situated in the country, well isolated and far removed from any sewers, was visited in May last by a severe outbreak of typhoid fever, and as there was no fever in the neighbourhood it seemed probable that the source was to be found on the spot. The well yielded water of a pleasant taste, perfectly clear, and colourless. Its analysis gave per million parts:—

Total solids.	Chlorine.	N as nitrates.	C. I.	Organic. II.	O of $KMnO_4$. consumed.
1378	326·6	26	2	1·8	0·186

The dissolved gases per litre were—

$$CO_2 = 58 \text{ c.c.} \quad O = 4 \text{ c.c.} \quad N = 15 \text{ c.c.}$$

When kept for a few days the water acquired an odour, and when this was rendered more sensible by warming in a flask it suggested the smell of putrid urine. This particular well was sunk in the court-yard of the establishment, and afterwards covered in. About 60 feet distant a cesspool had been constructed six feet deep. It had long been used, but for the last three years had received urine and soap-suds exclusively; from this the well is supposed to have received its pollution. After the outbreak of fever it was emptied and filled up. A bore-well 100 yards from the cesspool and in another direction, gave water of the following composition per million parts:—

Total solids.	Chlorine.	Ammonia.	N as nitrites and nitrates.	C. I.	Organic. II.
840	180	traces	5·5	2·9	2·8

Dissolved gases in a litre:—

$$CO_2 = 32·5 \text{ c.c.} \quad O = 3·5 \text{ c.c.} \quad N = 13 \text{ c.c.}$$

D. B.

South American Saltpetre. By G. Langbein (*Dingl. polyt. J.*, **232**, 453—460).—The author explains the formation of Peruvian saltpetre by the assumption that the nitrogen of rotting sea-weeds eliminated as ammonia was oxidised by the air into nitric acid, and that this, combined with the bases present in the sea-water, was concentrated by spontaneous evaporation.

The following is an analysis of the water used in Peruvian saltpetre works for feeding boilers, from which it will be seen that the water represents one of the worst kinds employed for such purposes:

Residue per liter in grams	5·8400	5·8600
$CaSO_4$	2·0606	1·9244
Na_2SO_4	1·4731	1·5620
$MgCl$	0·2256	0·2269
$NaCl$	2·0511	2·1332

This water is now purified by adding sodium carbonate to it in quantity equivalent to the lime and magnesia present, and agitating the mixture by means of a Körting's elevator. The magnesium carbonate is then decomposed with milk of lime, and the mixture allowed to settle.

With regard to the manufacture of saltpetre, various improvements have recently been made in boiling out the raw material. Instead of using direct steam, condensers are employed. These form closed square cylinders 12 m. × 1·85 m. × 1·85 m., into which the raw material is brought on perforated trucks, which run on rails. The

trucks and contents remain in the cylinders during the boiling out, and contain at the end of the operation the insoluble residue. The condensers are worked at a pressure of 4 to 5 atmospheres, agitation being procured by elevators.

In conclusion, analyses of the Peruvian raw material from various deposits are given. The most important deposits are those situated between Taltal and Paposa :—

$NaNO_3$.	NaCl.	$Na_2SO_4 + H_2O$.	$CaCO_3$ and insoluble.
47·2	7·4	26·7	18·7

The saltpetre deposits in Chili are almost unlimited in size, but the layer which yields saltpetre (caliche) is less extensive, its thickness being between 30 and 40 cm. D. B.

Chemical Technology of Glass. (*Dingl. polyt. J.*, **232**, 348—353).—Frickinger has observed that Bohemian glass bottles are attacked by sodium tartrate, magnesia, crystallised sodium carbonate, potassium carbonate, and by a mixture of camphor and alcohol.

Weber has undertaken a large number of experiments as to the chemical composition of glass and the resistance which it offers to atmospheric influences. He has investigated a series of good quality glasses, of defective glasses, and of glasses which can no longer be used practically, and therefore approach near to the defective series. Good glasses are those which are in good condition after being used for some time. According to Weber, their surface should not become covered with moisture when exposed to the air. Defective glasses show a greater tendency to take up moisture, and dirt adheres to them more easily. When they are treated with hydrochloric acid gas, a white stain is produced, whereas good glass remains unaltered.

In the paper, numerous analyses of various kinds of glass are arranged tabularly. These analyses show that the quality of glass depends no more on the absolute and often considerable quantity of silicic acid than on the small quantity of alkali present, but that, besides the correct proportion of silicic acid to the bases, the proportion of the lime or the oxide of lead and the alkalis influences the quality of the glass. Thus in the case of defective glasses, the proportion of silicic acid to the bases was less than 3 : 1, and the alkalis predominated over the lime. Although with good glasses, the proportion of silicic acid is often slightly less than that required, they always contain more lime than alkalis. D. B.

Phosphorus in Ancient Iron. By A. E. Arnold (*Chem. News.*, **40**, 138).—The following is an analysis of a scoria produced in Roman or Etruscan times from the specular ore of Elba :—

FeO.	Al_2O_3.	MnO.	CaO.	MgO.	ZnO.	S.	P_2O_5.	SiO_2.	O and undetermined.
76·49	2·57	0·60	1·32	0·64	0·20	0·40	0·34	14·20	3·88

It is of interest to note that the phosphoric acid is about eight times as much in the natural ore, which usually contains 0·04 per cent. P.

The author obtained in 1878 a piece of metallic iron from the same district. It gave on analysis :—

Combined carbon.	Graphite.	Si.	S.	P.	Mn.
0·873	2·853	0·544	0·096	0·090	0·091

Fe_2O_3.	Fe.	Moisture.
2·430	92·804	0·092

Cast-iron recently produced from Elba ore near the same locality contained three times the quantity of silicon present in the above analysis, the constituents being as follows :—

	C.	Si.	S.	P.	Mn.	Fe.	
I.....	4·306	1·672	0·067	0·110	0·748	93·256	= 100·159
II.....	4·147	1·676	0·056	0·108	0·757	93·256	= 100·000
Mean	4·306	1·674	0·067	0·109	0·753	93·256	= 100·165

D. B.

Dephosphorisation of Pig-iron. By Head (*Dingl. polyt. J.*, **232**, 451).—According to Thomas and Gilchrist it is possible to remove within half an hour the whole of the silicon and four-fifths of the phosphorus contained in Cleveland iron. The metal is exposed to a very strong blast in a furnace lined with dolomite and red ironstone. This discovery has been more fully developed by Bolckow, Vaughan, and Company, who at present prepare steel in the Bessemer converter from Cleveland iron, which surpasses in purity all other brands of cast-steel.

On account of the extremely high temperature which prevails in the converter during the blowing, it must be coated internally with a refractory material, a lining of pure quartz-sand (ganister) being used. The chemical action which is produced by the introduction of air into the fused metal is oxidation of all the substances mixed with the iron, besides oxidation of part of the iron itself. The silicon forms silicic acid, the phosphorus, phosphoric acid, and part of the iron, ferric oxide. The latter has two acids at its disposal —SiO_2 in considerable quantity and P_2O_5 in small quantity—the resulting product is iron silicate, whereas the phosphoric acid at the end of the operation is reduced and again enters the iron. A different result is however obtained if, besides ferric oxide, other bases are present in excess, or, in other words, if the lining of the converter consists of metallic oxides and not of silicic acid. Thomas and Gilchrist's discovery is based on this circumstance. For lining the converter a species of dolomite consisting of 7 per cent. SiO_2, 3·5 per cent. Al_2O_3 and Fe_2O_3; 88 per cent. $CaCO_3$ and $MgCO_3$ is used. This material is ground, pressed in moulds of 229 × 152 × 76 mm., and burnt strongly, so that all the carbonic acid escapes. The bricks are then fixed in the converter. Before charging the latter with the melted iron, a certain quantity of dolomite and red hæmatite is added, which dissolves in the metallic bath and protects the lining of the converter. After blowing for ten minutes with a blast of 755 mm. mercury, a further quantity of dolomite and hæmatite is added and the

blast continued for fifteen minutes. Finally fused specular iron is added, and after six minutes' blowing the operation is finished. The slag formed is basic, whilst hitherto it was always distinctly acid, and it is due to this circumstance that the phosphorus is absorbed by the slag.

The steel prepared from Cleveland iron with 1·5 per cent. phosphorus contained only 0·02 per cent., and gave very satisfactory results in all trials as to firmness. D. B.

Manufacture of Crucible Steel. By H. T. Bell (*Chem. News*, **40**, 102).—In giving an outline of the manufacture of steel by cementation, the author mentions that, after the converting process the bars of steel are covered with blisters, and in consequence of the various theories proposed to account for this peculiar formation, it was thought necessary to make a series of investigations. It was found that a marked increase of silicon was obtained where the blisters occurred, whilst the physical and chemical conditions had been changed. The iron had assumed a crystalline structure, and had chemically combined with a certain quantity of carbon. This latter change commences on the exterior, and extends itself to the interior of the bars, if the process be continued sufficiently long, thus showing that carbonic oxide never penetrates into the centre of the bar, until the whole is converted into steel. It is a remarkable fact that after the conversion of the iron, a quantity of the charcoal in the converting pots is found in a pulverised state, so as to be unfit for further use.

The most important of the elements which affect the quality and mechanical properties of steel are the following:—Carbon, silicon, sulphur, phosphorus, and manganese. The changes which take place when these elements are introduced are well known. D. B.

Analysis of Alloys Employed as Stopping for Teeth. By R. Bender (*Arch. Pharm.* [3], **14**, 403).—Blandy's patent "stopping" consists of tin 91·63 parts in 100, silver 3·82, and copper 4·4. This is in plates 3 mm. thick, whilst another alloy, which when mixed with mercury forms a hard amalgam, is a silvery-white powder, and consists of silver 48·33 parts in 100, tin 36·78, gold 14·72.

E. W. P.

Investigation of American and Russian Petroleum. By J. Biel (*Dingl. polyt. J.*, **232**, 354—363).—It is stated that the American petroleum springs, although more abundant, are poorer in petroleum than the Russian springs, the average yield of Russian springs being three times as large as that of American. In order to save the expense of plant, the Russian borings are only made 70 meters deep; while in America their depth is from 300 to 400 meters.

Some time ago, the author pointed out the superiority of Caucasian petroleum as compared with American petroleum. It is characterised by its entire absence of tarry substances, and has a greater illuminating power. At a meeting of English importers of petroleum held at Liverpool, the question as to the great alteration in the quality of American petroleum was discussed, when it was shown that the springs formerly worked have been nearly exhausted, and yield only about 25 per cent. of the total exports, the remainder being furnished

by the springs recently discovered in the Bradford district. The oil obtained from this district varies from the original petroleum in many respects. The danger of fire is much greater, as it ignites when warmed to 30°, and it burns very badly, as it contains a large quantity of heavy oils.

Although Russian petroleum is a purer product than American petroleum, its firing point is very low. This is due to the fact that the Russian manufacturers have endeavoured to imitate the specific gravity of American petroleum. The author mentions that unless the firing point is increased to 38° (the present firing point being 30°), Russian petroleum cannot compete with American in the European market. The reason that this has not yet been done is, that the Russian manufacturers believed that by altering the firing point the specific gravity would be increased so materially that the oil would lose its property of following the capillary attraction of the wick. The author has investigated this question more minutely, and found that the "drawing up" of petroleum is independent of the specific gravity, but varies with the boiling point; the lower the latter, the greater the tendency to follow the capillary attraction of the wick; moreover the firing point of petroleum does not depend on the specific gravity, but is regulated entirely by the boiling point of the oil.

D. B.

American Baking Powders and Alum. By H. A. Mott (*Analyst*, 1879, 143—146).—The author has examined a large number of baking powders, and found that most of them were largely adulterated. The best powders are composed of potassium bitartrate, tartaric acid, ammonium carbonate, and sodium bicarbonate, held together by a little starch to prevent decomposition. The injurious powders are composed of alum and sodium bicarbonate, and often contain "terra alba," insoluble calcium phosphate, &c.

The effect of alum on bread is to tend to whiten it, and to prevent an excess of fermentation (when yeast is used), when the altering gluten or cerealin acts too much on the starch, but whilst it accomplishes this object, it lessens at the same time the nutritive value of the bread by rendering the phosphoric acid insoluble. The effect of alum when taken internally has been shown by Wilmer and others, to produce dyspepsia, constipation, vomiting, griping, and even inflammation of the gastro-enteric mucous membrane, as it is a powerful astringent, acting chemically on the tissues.

The advantages of using "baking powder" in preference to yeast, are that with the former none of the nutritive parts of flour are destroyed, a larger yield is obtained, and the result accomplished with a great saving of time, which would otherwise be required to promote the fermentation when yeast is used. The advantage of using baking powder in preference to the ordinary cream of tartar and soda found on the market are not only that it is more economical, but that the results are always successful, there being no fear of producing an alkaline taste or yellow streaks in the product. D. B.

Arsenic in Grape-sugar. By Cloüet and Ritter (*Bied. Centr.*, 1879, 477).—The above investigators have independently found that

all commercial grape-sugar contains arsenic in small quantities; according to Ritter the amount varies from 0·0025 to 0·1094 gram per kilo. The arsenic is probably derived from the sulphuric acid used in the manufacture. J. K. C.

Experiments on the Fining of Wine. By E. Mach and Others (*Bied. Centr.*, 1879, 453—456).—The object of these experiments was to ascertain the quantity of tannin extracted from wine by various reagents, such as gelatin, isinglass, white of egg, skimmed milk, and sweet whey, the quantity of each used in the experiments being such that they contained the same fixed amount of nitrogen. Two wines, a red Teroldigo, and a white Nosiola, of the same age, were employed, the former containing 1·6 and the latter 0·21 per cent. of tannin. The results prove that the precipitate formed by each of the above reagents is richer in tannin the larger the quantity contained in the wine, but in no case can the whole of the tannin be extracted. The amount, however, precipitated per gram of reagent is smaller as the reagent is stronger. For example, a Teroldigo containing 4·8 per cent. of tannin lost 121·5 grams of tannin per hectolitre when cleared with 100 grams of gelatin, but when this was added in two parts of 50 grams each 126·3 grams of tannin were precipitated. It is also necessary that the fining reagent should be thoroughly mixed with the wine. Both wines lost 0·1 per cent. of tannin by treatment with 100 grams of aluminium phosphate per hectolitre, and the greatest loss of tannin caused by kaolin was 0·5 per cent. in the case of the white wine, and 0·3 per cent. in that of the red.

J. K. C.

Apple and Pear Wine. By C. Mader (*Bied. Centr.*, 1879, 477).—The author finds that the fermented juice prepared from apples and pears in the Tyrol contains from 5 to 6 per cent. of alcohol and about the same quantity of free acid. The quantity of alcohol is too small for the fermented juice to keep well. The author suggests the addition of pure sugar, and exposure of the solution to the air, to induce the separation of extractive matter. J. K. C.

Artificial Yeast for Molasses Distilleries. By A. Markl (*Bied. Centr.*, 1879, 456—459).—The author describes at some length the preparation of yeast from molasses and bran, the effect of which he compares with that of other yeasts. His experiments show that more sugar was decomposed in the same time by this than by any other ferment used. J. K. C.

Analyses of Water for Brewing. By Krandauer (*Bied. Centr.*, 1879, 446).—The quantity of solids in solution in the 52 waters examined ranged from 8 to 92 parts per 100,000, thirty samples ranging from 20 to 50. The quantity of chlorine present was from 0·02 to 40·7 parts, in 39 cases the chlorine not being more than 9·5. As regards organic matter, most of the waters could be considered good. The lime and magnesia were determined in 36 cases, in 34 of which the former varied from 1·1 to 16·3 parts, amounting only in

two cases to over 23. The magnesia ranged from 0·06 to 8·7 parts per 100,000. J. K. C.

Remarks on Beer Fermentation. By P. Müller and Hauer (*Bied. Centr.*, 1879, 462—463).—The authors enlarge on the importance of examining yeast for cells of *Saccharomyces exiguus*, as the presence of these causes an after fermentation highly injurious to the taste of the beer. J. K. C.

Researches on Beer. By G. Holzner and Others (*Bied. Centr.*, 1872, 450—452). The most important result noted in the paper is that the amount of phosphoric acid in beer is no criterion of its quality. The analyses of 25 samples of beer is given in a tabular form. J. K. C.

Explosion of the Flour Mills at Minneapolis, Minnesota. By S. F. Peckham (*Chem. News*, **40**, 59—61).—In describing the explosion of the flour mills at the above place the author mentions that, although his point of observation was about a mile distant, he heard a noise that sounded as if something as heavy as a barrel of flour had been tipped over immediately above the floor of the room he occupied. A few seconds later the sound was repeated, and in less than two minutes from the time of the first explosion, the elevator, which was 108 feet high, was wrapped in flames from top to bottom, while in five minutes, six flour mills, the elevator, a machine shop, blacksmith's shop, and planing mill, with a number of empty and loaded cars, were in flames. The enormous and sudden displacement of air which followed the explosion, and the tremendous force which was consequently exerted laterally, was shown in the condition of the roundhouse of the railroad forty or fifty feet from the mills. The sills were drawn out towards the mill until the building, which was a wooden structure, burst, letting a part of the roof fall in and leaving the sides standing at a sharp angle. On the river at the water's edge a displacement of the water, producing a wave estimated to be eighteen inches high, was noticed before the report of the explosion was heard.

As to the causes of the explosion, various theories have been proposed. The author mentions that there is but little doubt that in any flour mill sufficient dust accumulates upon beams and machinery to produce an explosive atmosphere, if from any cause this dust is scattered into the air and flame is communicated to the mixture while the dust is suspended. A number of experiments showed that the wheat enters the stones from the dryers at a temperature of 100° F., and that it leaves the stones at 120—130°. The temperature of the ground middlings as it left the stones averaged about 10° higher. It is the concurrent testimony of millers and millowners that dry stones are of comparatively frequent occurrence, and that they are practically unavoidable. Obstruction of the feed from any one of a number of accidental causes will produce dry stones. The danger arises from the friction of the stones heating the last portion of the grist that remains between the stones to a temperature sufficient to char it or

convert it into a substance resembling tinder, which would readily ignite from a spark produced by the stones striking together. Another source of danger arises from nails or gravel passing between the stones with the grist and increasing the friction. The problem therefore for the consideration of millers, &c., is how to prevent or detect dry stones, particularly those used for grinding middlings, it having been urged that the formation of dry stones can hardly be avoided by any amount of care. D. B.

Explosion of Nitromannite. By N. Sokoloff (*Deut. Chem. Ges. Ber.*, **12**, 688).—A perfect explosion of moist pyroxylin containing 25 per cent. of water is induced by the explosion of 2 grams of nitromannite enclosed in a capsule. The explosion of nitromannite can be effected by the explosion of 0·2 gram of mercury fulminate or diazobenzene nitrate. The same effect is produced by the detonation of more than 1 gram of potassium picrate or potassium chlorate.

G. T. A.

The Proper Time for Pressing Olives. By Bechi (*Bied. Centr.*, **8**, 309).—The author finds that olives which have lain two months after being gathered contain 4·6 per cent. more oil than the freshly gathered fruit. J. K. C.

Extinguishing Fires in Tar Distilleries. By W. Smith (*Chem. News*, **39**, 190).—The author has found the crude ammonia water known as gas-liquor to be very efficacious in extinguishing the fire from burning pitch, although water alone seemed to have no effect. He therefore recommends that the supply of gas-liquor in tar distilleries should be so disposed as to be available for extinguishing fires in any part of the works, and that owners of cotton mills, &c., should erect tanks furnished with supply pipes, and keep a suitable stock of the liquor on hand. J. M. H. M.

Salicylic Acid as a Preventative of House-fungus. By F. Falsky (*Bied. Centr.*, 1879, 465).—The author recommends an alcoholic solution of 5 grams salicylic acid per litre, which entirely destroys the fungus and prevents its reappearance in places which have been washed with the solution. J. K. C.

Method of Preventing House-fungus. By H. Zerener (*Bied. Centr.*, 1879, 480).—The author uses either waterglass or infusorial earth, to which 6 per cent. of salt and 3 per cent. of boric acid have been added. J. K. C.

INDEX OF AUTHORS' NAMES.

ABSTRACTS. 1879.

A.

Abel, F. A., recent contributions to the history of detonating agents, 846.

Abel. See also Noble.

Abt, A., continuous spectrum of the electric spark, 765.

Adam, A., new and rapid process for analysis of butter, 80.

Adams, F. D., presence of chlorine in scapolites, 697.

Ador, E. A., and J. M. Crafts, action of phthalic anhydride on naphthalene in presence of aluminium chloride, 940.

Ador, E., and A. Rilliet, hydrocarbons produced by the action of methyl chloride on benzene in presence of aluminium chloride, 228, 527.

Ador. See also Friedel.

Adrianowsky, A., action of acetic and sulphurous anhydrides on aluminium chloride, 620, 915.

Albert, H., and L. Siegfried, estimation of the value of superphosphates, 967.

Allen, A. H., distinctive tests for phenol, cresol, and creosote, 182.

—— petroleum spirit and benzene, 1063.

—— presence of nitrogen in steel, 1017.

Allihn, F., compounds of ethyl monochloracetoacetate, 915.

Amayat, E. H., compressibility of gases at high pressures, 1004.

Andreasch, R., ash of the garden pink and rose, 338.

—— decomposition of ammonium formate by heat, 705.

Andreoni, G., nicotine, 731.

Andrews, T., curious concretion-balls derived from a colliery mineral water, 1024.

Annaheim, J., tetranitro-oxysulphobenzide, 244.

Anschütz, R., action of ethyl iodide on the silver salts of maleic and fumaric acids, 223.

Anschütz, R., and L. P. Kinnicutt, phenylglyceric acid, 644.

Anschütz, R., and G. Schultz, phenanthrenequinone, 538.

Ansdell, G., physical properties of liquid acetylene, 1028.

Arata, P. N., alkaloïd of *Baccharis cordifolia*, 1045.

Arnold, A. E., phosphorus in ancient iron, 1074.

—— solubility of stannic oxide in hydrochloric acid, 888.

Aronheim, B., action of nitrous acid on resorcinol ethers, 465.

—— action of nitrous acid on stannic phenyl chloride, 651.

—— on Schützenberger's chlorine and iodine acetates, 452.

—— synthesis of the compounds of phenyl with tin, 249.

Arzruni, A., crystallographical and chemical examination of some arsenical pyrites, 900.

Aschenbrandt, H., paradiethylbenzene from paradibromobenzene, 920.

Attenkofer, G., a simple gas-holder, 877.

Auerbach, F., the passage of the galvanic current through iron, 686.

Austen, P. T., on dinitroparadibromobenzenes and their derivatives, 50.

Ayrton, W. E., electrical properties of bees' wax and lead chloride, 427.

B.

Babcock. See Hübner.

Baeyer, A., action of phosphorus pentachloride on isatin and allied compounds, 535.

—— diphenylphthalide and phenylphthaleïn, 636.

Baeyer, A., synthesis of chinoline, 946.
—— the indigo-blue group, 937.
Balbiano, L., *a*-isochlorobutyric acid and its derivatives, 615.
Balland, waters of the Chéliff, 699.
Ballo, M., action of dehydrating agents on camphoric and camphoramic acids, 539.
—— mineral waters of Buda-Pesth, 125.
Balsohn, M., action of ethylene on benzene in presence of aluminium chloride, 785.
Baltus. See Béchamp.
Bancel, C., and C. Husson, phosphorescence of lobster's flesh, 665.
Bandrowski, E., reaction of dibromosuccinic acid with water, 523.
Bantlin, A., metanitrophenol and its derivatives, 237.
Barbieri, J., albuminoïds of gourd seeds, 272.
Barbieri. See also Schulze.
Bardy, C., and L. Bordet, estimation of methyl alcohol in wood spirit, 487.
—— —— preparation of methyl formate and pure methyl alcohol, 520.
Barth, L., dioxybenzoic acids, 157, 644.
—— thymoloxycuminic acid, 158.
Barth, L., and G. Goldschmidt, ellagic acid, 930.
Barth, L., and M. v. Schmidt, derivatives of *a*-phenoldisulphonic acid, 933.
Barth, L., and J. Schreder, action of fused soda on phenol. Synthesis of phloroglucinol, 633.
—— —— diphenol, 64.
—— —— fusion of aromatic acids with soda, 926.
—— —— oxidation of resorcinol to phloroglucinol, 633.
Barral, J., nitrates in beet-roots, 337.
Barsylowsky, azo-derivatives of toluene, 237.
Barus, C., the thermoelectric position and electric conductivity of steel in their relation to hardness, 999.
Baubigny, H., the oxide of nickel, Ni_3O_4, 299.
Baudrimont, A., influence of coloured light on the evaporation of water, 863.
Bauer, M., the crystal system of potash mica, 24.
—— the hydrohæmatite of Neuenberg, 604.
Baumann, E., behaviour of phenol in the animal organism, 816.
—— hydrogen-phenol sulphate and similar derivatives of the phenols, 148.
Baumann, E., and L. Brieger, formation of cresols during putrefaction, 789.
—— —— paracresol, 789.
Baumann, E., and C. Preusse, bromophenolmercapturic acid, 803.
—— —— oxidation and synthesis in the animal organism, 814.
Baumann, E., and F. Tiemann, constitution of indigo, 806, 935.
Baumhauer, H., "etch figures" on quartz crystals, 439.
Baur, A., dimethylparaphenylenediamine thiocarbamide, 628.
Bayley, T., analysis of alloys containing copper, zinc, and nickel, 485.
—— catalysis, 501.
—— complex oxides of cobalt and nickel, 507.
Beamer, M., and F. W. Clarke, aniline salts, 785.
—— —— lithium picrate, 789.
Béchamp, A., formation of carbonic anhydride, alcohol, and acetic acid by yeast alone in presence and absence of oxygen, 663.
—— influence of oxygen on alcoholic fermentation, 735.
Béchamp, J., nature of the albumins in hydrocele, 550.
Béchamp, J., and E. Baltus, modification effected by the animal organism on various albuminoïd substances when injected into the veins, 334.
Bechi, the proper time for pressing olives, 1080.
Bechi, G. v., new mode of formation of ketones, 529.
—— succinyl compounds of the toluidines, 461, 527.
Beck, C., dioxydiphenylmethane, 324.
Becker, G. F., reduction of weighings in air in chemical analysis to a vacuum, 396.
Beckmann, E. O., oxidation of products of diethyl sulphide and analogous compounds, 37.
Beckurts, H., and R. Otto, mode of action of sulphuric monochloride, 229.
—— —— sulphuric monochloride and dichloride, 200.
—— —— synthesis of aromatic sulphones, 242.
Becquerel, E., on a note by Lamansky on Stokes's law, 862.
Becquerel, H., magnetic rotatory power of gases at ordinary temperatures and pressure, 576.
Beetz, W., conductivity of liquids for heat, 1001.
—— electric conductivity of zinc sulphate solution, 804.

Beetz, W., excitation of electricity by the contact of solid and gaseous bodies, 348.
Beilstein, F., perchlorophenol chloride, 463.
—— separation of zinc from nickel, 276.
Beilstein, F., and L. Jawein, estimation of cadmium, 746.
—— —— estimation of zinc, 672.
—— —— treatment of Bunsen's cells, 576.
Beilstein, F., and A. Kourbatoff, dinitrochlorobenzene, 376.
—— —— nitrophthalic acid obtained by oxidation of nitronaphthalene, 644.
—— —— oxidation of bromonaphthalene, 807.
—— —— oxidation of nitronaphthalene, 722.
—— —— action of hydrogen sulphide on certain nitro-compounds, 230.
—— —— chloranilines, 143.
—— —— chloronitranilines, 309.
—— —— formation of chlorophenylenediamine, 144.
Beketoff, M., determination of the atomic heat of hydrogen in its combination with palladium, 590.
—— heat of hydration of sodium oxide and the action of sodium hydroxide and of hydrogen on sodium oxide, 689.
Bell, C. A., pyrrol derivatives, 525.
Bell, C. A., and E. Lapper, dry distillation of ammonium salts of saccharic acid, 524.
Bell, C. J., action of phosphorus pentachloride on saccharic acid, 917.
Bell, H. L., manufacture of crucible steel, 1076.
Bell, J. L., separation of carbon, sulphur, and phosphorus in the open hearth, puddling furnace, and Bessemer-converter, 185.
Bellucci, supposed existence of hydrogen peroxide in the organism of plants, 665.
Bemmelen, J. M., absorptive power of soils and of silica, 339, 552.
Bender, R., analysis of alloys employed as stopping for teeth, 1076.
Bendix, J., derivatives of ortho-nitrophenol, 314.
Benedikt, R., pentabromoresorcinol, 55, 464.
—— tribromophenol bromide and tribromoresorcinol bromide, 717.
—— trinitroso- and trinitro-phloroglucin, 57.
Benedikt. See also Weselsky.
Beins, H., preparation of carbonic anhydride under any desired pressure, 676.
Bennett, W. Z., and H. B. Hill, dichloracrylic acid, 616.
Benrath, H. E., Macagno's investigations on bottle-glass, 562.
Berend, L., isodulcite, 40.
Bernheimer, O., organic ferricyanogen compounds, 611.
Bernthsen, amidines and thiamides of monobasic organic acids, 922.
Bernthsen, A., and H. Klinger, sulphine compounds of thiocarbamide, 650.
Bernthsen, A., and H. Trompetter, amidines and thiamides of monobasic organic acids, 146.
Bersch, J., cultivation of pure beer-yeast, 1046.
Bert, P., region of the solar spectrum which is indispensable to vegetable life, 336.
Berthelot, action of organic solvents on sulphur and on metallic sulphides, 771.
—— amalgams of the alkali-metals and the nascent state, 864.
—— changes which wine undergoes when kept, 763.
—— chemical constitution of amalgams of the alkali-metals, 883.
—— combination of carbonic oxide with the elements, 591.
—— decomposition of haloïd acids by metals, 589.
—— direct combination of cyanogen with hydrogen and the metals, 909.
—— etherification, 866.
—— explosive mixtures of air with combustible powders, 412.
—— formation of haloïd ethers in the gaseous state, 435.
—— heat of formation of cyanogen, 767.
—— hydrogenation of benzene and aromatic compounds, 376.
—— influence of metallic chlorides on etherification, 449.
—— observations on Noble and Abel's memoir on the combustion of gunpowder, 875.
—— ozone and the silent electric discharge, 435.
—— oxidation of nitrous acid by ozone and by moist oxygen, 9.
—— reaction between mercury and hydrochloric acid gas, 298.
—— reciprocal displacements between oxygen, sulphur, and the halogens when combined with hydrogen, 296.
—— relative affinities and reciprocal

displacements of oxygen and the halogen elements, 351.
Berthelot, remarks on a note on chloral hydrate by Wurtz, 1006.
—— some thermochemical data, 874.
—— transformation of sugar into alcohol by a purely chemical method, 778.
Bertram, J., excretion of phosphoric acid by herbivora, 392.
Bertrand, E., cinnabar crystals from California, 440.
—— the crystal form and twin-formation of leucophane, 442.
Berwerth, F., examination of lithiamica from Paris (Marne), Rozena, and Zinnwall, 23.
Beyrich, C., process for bleaching vegetable fabrics, 761.
Bichat, E., magnetic rotatory power of vapours, 577.
Biefel. See Poleck.
Biel, J., investigation of American and Russian petroleum, 1076.
Biermann, E. W. L., manganese alloys, 186.
Binder, F., dimethylparaphenylenediamine carbamides, 627.
Binder. See also Fittig.
Bindschedler and Busch, manufacture of resorcinol, and of eosin and other derivatives of resorcinol, 291.
—— —— new fast green, or malachite green, 571.
Bischof, G., estimation of traces of lead, 402.
—— sanitary notes on potable water, 985.
Bischoff. See Hilger; also Wallach.
Blankenhorn, A., aëration of must, 492.
Blankenhorn, A., and H. W. Dahlen, fermentation of must, 993.
Blankenhorn. See also Gamgee.
Blas, M., detection of salicylic acid in beer, 342.
Blattner. See Michler.
Bleibtreu. See Wallach.
Bleunard, A., action of trimethylamine on carbon bisulphide, 305.
Blondlot, R., capacity of voltaic polarisation, 864.
Blumberg, T., contributions to a knowledge of the alkaloïds of ergot, 269, 387.
Blyth, A. W., composition of Devonshire cream, 1068.
Bochmann, Chili saltpetre as a manure for barley, 1050.
Bochmann. See also Döring.
Bode, F., extraction of copper by wet processes, 757.
Boeck. See Liebermann.
Böhm, J., formation of starch in chlorophyll grains in absence of light, 551.
Böttger, R., crystalline structure of bees' wax, 171.
—— detection of gypsum, heavy spar, &c., in meal, 183.
—— formation of hydrogen peroxide by the explosion of a mixture of oxygen and hydrogen, 103.
—— Planté's secondary battery, 101.
—— preparation of salts in a finely divided state, 107.
—— production of a high temperature by means of ammonium nitrate, 102.
—— production of rotatory movements in mercury, 102.
—— pyrophoric iron, 119.
—— reagent for detecting nickel, 179.
—— steeling copper-plates, 186.
Böttinger, C., a new base, $C_{19}H_{18}N_2$, 716.
—— acetylene-carbamides, 142.
—— action of aniline on glyoxylic acid, 51.
—— action of phosphorus pentasulphide on organic acids, 45.
—— benzal sulphide and thiobenzaldehyde, 791.
—— conversion of aldehyde into mercaptan, 451.
—— dissociation of ammonium chloride, a lecture experiment, 196.
—— glyoxylic acid, 619.
—— monosulpholactic acid, 45.
—— pyroracemic acid, 524.
—— the amount of water contained in crystallised calcium glycollate, 522.
—— thioglycolic and thiodiglycolic ethers, 138.
Bohlig, E., water analysis, 963.
Boisbaudran, L. de, samarium, a new metal from samarskite, 889.
—— spectrum of erbium nitrate, 862.
—— spectrum of ytterbium, 861.
Boisbaudran. See also Smith, J. L.
Bokay, A., digestibility of nucleïn and lecithin, 814.
Bordet. See Bardy.
Borgmann. See Neubauer.
Bornträger, A., a new indicator for use in acidimetry and alkalimetry, 396.
—— method for rapidly incinerating meal, 282.
Bottomley, J., colorimetrical experiments, 77.
Bouchardat, G., formation of glycollic and pyruvic acids from tartaric acid, 916.
—— identity of the hydrates of di-isoprene, caoutchene, and terpene, 1039.

Bouchut. See Wurtz.
Bourgeois, L., crystalline barium chromate, 437.
Bourgoin, E., bromocitraconic acid, 457.
—— elimination of bromine from bromocitraconic acid, and a new organic acid, 1037.
Boussingault, chromium-steel, 286.
—— composition of the milk of the cow-tree, 73.
Boutmy, H., researches on nitroglycerol, 1032.
Bouty, pressure produced by galvanic deposits, 576.
Bouvet, A., electrochemical actions under pressure, 293.
Braun, F., unipolar electrolytic conduction, 194.
Bremer. See Mulder.
Breuer, A., and Zincke, derivatives of the hydrocarbon, $C_{16}H_{12}$, from phenol glycol, 327.
Brieger, L., aromatic products of the putrefaction of albumin, 806.
Brieger. See also Baumann.
Briem, H., influence of light on the yield of sugar beets, 1047.
Briem. See also Liebscher.
Brimmer, C., action of rain on clover hay, 823.
Brögger, W. C., occurrence of thomsonite at Läven, 605.
—— the crystal system of mosandrite, 608.
Bronner, use of Hempel's lamp for illustrating silver assay as a lecture experiment, 402.
Brown, J., theory of voltaic action, 426.
Brown, W. G., philippium, 204.
Brühl, J. W., limits to the application of the method of determining vapour-densities in the barometric vacuum, 499.
—— preparation of divaleryl, 520.
—— purification of mercury, 508, 602.
Brunner, H., desoxalic acid, 619.
—— improvements in the manufacture of alkali, 422.
Brush, G. J., and E. S. Dana, a new and remarkable mineral locality in Fairfield Co., Connecticut, U.S.A., 891.
—— —— new minerals from Fairfield Co., Connecticut, 20.
Bruylants. Essence of rosemary, 725.
Buchka, K., reduction of acetophenone, 61.
Buchner. Adulteration of bees' wax, 675.
Büchner, E. W., red and yellow ultramarine, 885.
Büchner, E. W., ultramarine, 597.
Büchner and Tschermak, the meteoric iron of Hungen, 366.
Bührig, H., cerium aniline black, 682.
Buisine. See Duvillier.
Bunge, G., behaviour of potassium salts in the blood, 816.
Bunge, N., composition of beetroot gum, 912.
Bungener. See Graebe.
Burger, H., spectroscopic investigation of the constitution of liquids, 101.
Burger. See also Liebscher.
Burghardt, C. A., occurrence of dioptase on chrysocolla from Peru, 30.
—— the origin of some ores of copper, 17.
Buri, E., Japanese wax, 1037.
Busch. See Bindschedler.
Byk, S., removal of sulphur from guanidine thiocyanate, 614.

C.

Cahours, A., iodides of stannopropyl, 622.
Cahours, A., and E. Demarçay, acids obtained by distilling the crude acid from the saponification of fats in a current of steam, 1036.
—— —— iodides of stannobutyl and stannamyl, 919.
—— —— stannopropyls and stannisopropyls, 918.
Cahours, A., and A. Etard, a new nicotine derivative, 732.
Cailletet, L., compressibility of gases, 429.
—— a test for tartaric acid, which distinguishes it from citric acid, 674.
Calm, A., constitution of parabanic acid, 620.
—— vapour-density of aqueous acids with constant boiling points, 579.
Cameron, C. A., amount of solids in milk, 490.
—— estimation of lead as lead iodate, 484.
—— preliminary notes on the absorption of selenium by plants, 955.
—— the varying composition of well water, 485.
Cannizzaro, S., and Carnelutti, two isomerides of santonin, 330.
Cannizzaro, S., and L. Valente, santonin derivatives, 331.
Carnelley, T., relation between the melting-points of the elements and their coefficients of expansion by heat, 588.

Carnelutti. See Cannizzaro.
Carnot, A., mallardite, a new natural manganèse sulphate; and luckite, a new variety of iron sulphate, 901.
—— use of sulphuretted hydrogen in the dry way in analyses, 963.
Caro, H., and C. Graebe, rosolic acids, 59.
Caro, H., and Schraube, phenoldiazobenzene, 148.
Casamajor, P., influence of temperature on the deviation of polarised light by solutions of inverted sugar, 832.
Castan, F., estimation of minute quantities of soda in potassium nitrate, 399.
Cazeneuve, P., detection and estimation of salicylic acid in animal secretions, 488.
—— estimation of glucose in the blood, 557.
—— separation and estimation of hippuric acid, 748.
Cech, C. O., preparation of rosemary oil, 97.
Chapuis and Linnossier, presence of lead in bismuth subnitrate, 80.
Christiani, W., effect of manure on crops, 826.
Church, J. A., combustion in the blast-furnace, 841.
Ciamician, G., influence of temperature and pressure on the spectra of vapours and gases, 101, 685.
—— reduction-products of Elemi-resin with zinc-dust, 69.
—— spectra of the elements and their compounds, 685.
Claesson, P., ethereal sulphates of polyhydric alcohols and carbohydrates, 1033.
—— methyl and ethyl sulphates, 775.
Claisen, L., amides of phenylglyoxylic acid, 649.
—— benzoic cyanide and phenylglyoxylic acid, 647.
Claisen, L., and F. H. Morley, new method of preparing phenylglyoxylic acid, 322.
Claisen, L., and J. Shadwell, synthesis of pyroracemic acid, 45.
—— —— synthesis of isatin, 534.
Clarke, F. W., electrolytic estimation of mercury, 976.
—— specific gravity determinations, 295, 1004.
Clarke, J. W., some selenocyanates, 35.
Clarke. See also Beamer.
Classen, A., a new quantitative analytical method of manifold application, 969.
Classen, A., estimation of cobalt, nickel, and zinc by precipitation as oxalates, 1054.
—— new method of separating ferric and aluminium oxides from manganese, 1055.
—— separation of manganese from zinc, 1055.
Claus, A., cinchona alkaloïds, 168.
Claus, C. F., improvements in the manufacture of sulphide and other compounds of zinc, and in the production of bye-products resulting therefrom, 423.
Claus. See also Wallace.
Clausius, R., the relation between work effected by the diffusion of gases and the second law of thermodynamics, 3.
Clausnizer, F., action of sulphuric monochloride on the chlorides of titanium, antimony, tin, and silicon, 201.
—— experiments on the preparation of sulphuric bromide and sulphur tetrabromide, 354.
—— sulpho-oxychlorides, 691.
—— sulpho-selenium oxytetrachloride, 201.
Clermont, P. de, action of ammoniacal salts on metallic sulphides, and its application to mineral analysis, 672.
Clermont, P. de, and J. Frommel, aurin, 789.
—— dissociation of metallic sulphides, 13.
—— magnesia as an antidote for arsenious acid, 77.
Cleve, P. T., chlorostannates of the rare earths, 601.
Cloüet and Ritter, arsenic in grape-sugar, 1077.
Cochin, D., non-existence of a soluble alcoholic ferment, 1046.
Cocx, L. C. W., solubility of lime in water in reference to the prescription for *Aqua phagedænica*, 491.
Cöllen, T., sulphoparachlorobenzoic acid, 155.
Cohen, E., the meteorite of Zsádany, Temesvar, 609.
Collins, J., duporthite, a new asbestiform mineral, 24.
Conrad, M., ethyl formyltricarbonate, 918.
—— identity of acetopropionic acid and levulinic acid, 453.
—— substituted malonic acids, 707.
Conroy (Sir J.), the light reflected from potassium permanganate, 425.
Cooper. See Wanklyn.
Coppet, L. C. de, heat developed by

contact of water with anhydrous sodium sulphate, 589.
Coquillon, J., action of aqueous vapour on carbonic oxide in presence of red hot platinum, 880.
—— action of platinum wire on hydrocarbons, 302.
Corenwinder, B., on the banana, 479.
Corne, J., reduction of iodates by phosphorus, 103.
Cornu, A., ultra-violet limit of the solar spectrum, 861.
Cossa, A., cinder and lava from Etna, 904.
—— distribution of cerium, lanthanum, and didymium, 695.
—— serpentine from Verrayes (Aosta), 362.
Costello, D., gamboge, 1041.
Cotte, E., improvements in the manufacture of certain explosive compounds, 422.
Cottu, H., use of sour food for cows, 1049.
Councler, C., boron compounds, 621.
Crafts. See Ador; also Friedel.
Credner, H., the red gneiss of the Saxon Erzgebirge, 361.
Cresti, L., gas regulator for air-baths, 294.
Crié, L., an amyloid substance peculiar to the "asques" of pyrenomycetes, 613.
Croll, A. A., improvements in the manufacture of sulphate of alumina, 423.
Crookes, W., illumination of the lines of molecular pressure and the trajectory of molecules, 573.
Cros, C., action of light of different colours on silver bromide impregnated with various organic colouring matters, 504.
Crova, A., spectrometric measurement of high temperatures, 293.
Cumenge, E., and E. Fuchs, the state in which the precious metals exist in certain minerals, rocks, and artificial products, 509.
Custer, E., action of ethyl chlorocarbonate on mono- and di-amylamine, 913.

D.

D'Abbadie, amount of nitric acid in the waters of the Nile, 905.
Dahlen. See Blankenhorn.
Dahll, T., norwegium, a new metal, 890.
Dal Sie, G., active principle of insect powder, 807.
Dale, R. S., and C. Schorlemmer, aurin, 58, 925.
Damm. See Staedel.
Damour. See Descloiseaux.
Dana. See Brush.
D'Arsonval, estimation of sugar in blood, 674.
Dastre, "starch granules" and "amyloides" of the egg, 662.
Daubrée, A., a meteorite belonging to the eukrite group, 610.
—— experiments on the erosive action of strongly compressed hot gases, with reference to the history of meteorites, 1024.
David. See Prunier.
Davis, T. H., testing and valuing gas liquor, 79.
Davy, E. W., nitrification, 1046.
Debray, H., peculiarity of an experiment of Gay-Lussac and Thénard, 887.
Debrunner, H. G., third form of carbon in steel, 842.
De Chaumont, F., experiments with animal charcoal, silicated carbon, and spongy iron filters, 986.
De Forcrand, formation of glycocine from ethyl nitroacetate, 621.
—— formation of organic ultramarines, 622.
Dehérain, assimilation of soda by plants, 666.
Dehnst. See Liebermann.
Deite, C., ghea butter, 568.
—— iodine industry in France, 283.
—— testing lubricating oils, 188, 292.
Delachanal. See Vincent.
Delafontaine, M., decipium, a new metal from samarskite, 117.
—— philippium, 116.
—— terbium and its compounds, and the probable existence of a new metal in the samarskite of North Carolina, 114.
—— the mosandrum of J. L. Smith, 117.
—— the probable compound nature of the didymium from cerite, 119.
Demarçay, E., homologues of oxyheptic acid, 458.
—— relations of tetric and oxytetric acids and their homologues to succinyl, malyl, and other radicles of the bibasic acids, 459.
—— tetric acid and its homologues, 457.
Demarçay. See also Cahours.
Demel, W., amidonitrosulphide of iron, 597.

Demel, W., zinc phosphates, 1016.
—— zinc and cadmium arsenates, 884.
De Mering. See Musculus.
Demole, E., formation of a ketone containing four carbon-atoms from dibromethylene, 220.
Dennstedt, M., benzyl orthothioformate, 318.
Denzel, J., nomenclature and boiling points of the chlorobromo substitution products of ethane and ethylene, 368.
Desains, P., refraction of invisible heat, 864.
Descamps, A., potassium cobaltocyanide, 303.
Descloiseaux and Damour, homilite, 32.
Destrem, A., cholic acid, 333.
—— compounds of metallic salts with compound ammonias, 376.
Destrem. See also Schützenberger.
Deutsch, A., ethereal salts of tribasic formic acid, 453.
Dieck, E., and B. Tollens, the carbohydrates of the Jerusalem artichoke, 778.
Diehl, T., and V. Merz, naphthopicric acid and some of its derivatives, 250.
Dietzell, B. E., and M. G. Kressner, estimation of phosphoric acid in fish guano, 968.
—— —— testing of butter, 407.
Dieulafait, L., distribution of copper in primordial rocks, and in the sedimentary deposits derived from them, 1020.
—— —— presence of ammoniacal salts in sea-water, 9.
—— the existence of barium and strontium in all rocks constituting the primary formation, 444.
Disqué, L., urobilin, 170.
Ditte, A., action of hydracids on mercuric sulphate and of sulphuric acid on the haloïd salts of mercury, 299.
—— researches on the decomposition of metallic salts, and on certain inverse reactions which take place in presence of water, 1006.
Dittler. See Michaelis.
Dittrich, E., methyltaurine, methyltaurocyamine, and taurocyamine, 225.
Dixon, W. A., metallurgy of nickel and cobalt, 285.
—— extraction of gold, silver, and other metals from pyrites, 288.
Doebner, O., homologous tertiary diamines obtained in the methylaniline manufacture, 786.
—— malachite-green, 312.
Doebner, O., and W. Stackmann, synthesis of oxyketones by introducing acid radicles into phenols. Part II, 319.
Doebner, O., and W. Wolff, synthesis of oxyketones, 638.
Doelter, C., diopside, 442.
—— estimation of ferrous oxide in silicates, 484.
Doering and Bochmann, effect of artificial manures on the growth of barley and on meadow land, 828.
Dogiel, J., reactions of albumin, and behaviour of the albumin of the refracting media of the eye, 834.
Donath, E., applications of glycerol in analysis, 178.
—— detection of chromates and of free chromic acid, 401.
Donath, J., preparation of barium from barium amalgam, 691.
—— specific heat of uranoso-uranic oxide and the atomic weight of uranium, 688.
Dorn, E., electric currents produced by the flow of liquids through tubes, 346.
van Dorp. See Hoogewerff.
Douglas, T., green pigment from barium chromate, 987.
Dragendorff and Stahre, chemistry of the *Pæonia peregrina*, 1043.
Draper, J. C., presence of dark lines in the solar spectrum which correspond closely with the oxygen lines, 997.
Drechsler, G., potato cultivation, 823.
Dreschel, E., preparation of crystalline albumin compounds, 950.
Drevermann, A., recovery of sugar from calcium saccharates, 492.
Drevermann. See also Steffens.
Drown, T. M., determination of silicon in pig iron and steel, 974.
Drygin, a new quinine salt, 169.
—— cinchonicine, a new quinine alkaloïd, 169.
Duclaux, E., ripening and decomposition of cheese, 858.
Duke Carl Theodor of Bavaria, influence of the temperature of the surrounding air on the excretion of carbonic acid and the absorption of oxygen in the cat, 74.
Duncan, J., J. A. R. Newlands, and B. E. R. Newlands, improvements in the treatment of saccharine substances or compounds (patent), 421.
—— —— improvements in the treatment of sugar (patent), 421.
Dupré, A., detection and estimation of alum in wheat flour, 483.
Du Puy, C. M., direct process for making wrought iron and steel, 565.

Durand, bark of the root of the pomegranate, 169.
Durin, inversion of cane-sugar, and consecutive alteration of the glucosides so formed, 369.
Du Roi. See Kirchner.
Duvillier, E., derivatives of normal methoxybutyric acid, 523.
—— dimethacrylic acid, an isomeride of angelic acid, 782.
—— isomeride of angelic acid, 706.
Duvillier, E., and A. Buisine, commercial trimethylamine, 912.
—— —— separation of ethylamines, 306.
Dwars, B. W., determination of quinine in certain of its salts, 488.
—— on the iodosulphates of the quinine alkaloïds, 982.

E.

Ebermann. See Wein.
Eckart. See Heyden.
Eder, J. M., behaviour of gums and carbohydrates towards chromates under the influence of light, 911.
—— estimation of nitric acid in well water, 274.
—— examination of Chinese tea, 851.
Edison, T. A., action of heat on metals in a vacuum, 1018.
Edlund, E., the electromotive force produced by the flow of liquids through tubes, 998.
Egger, E., bilic acid, an oxidation-product of cholic acid, 810.
Elder. See Rodwell.
Eltekoff, reactions of the halogen-compounds of the olefines, 35.
Eltekoff. See also Lagermark.
Emmerling, O., metallic phosphides, 508.
Engel, R., and Moitessier, dissociation of ammonium hydrosulphide, 979, 880.
—— —— dissociation of ammonium sulphide, 879.
—— —— dissociation of chloral hydrate, 500.
Engelbrecht. See Ladenburg.
Engler, C., a sulphuretted derivative of acetophenone, 61.
—— sulphuretted derivatives of benzophenone, 61.
—— tetraphenylethane, 68.
Erdmann, J., colouring matter of red wine, 171.
Erlenmeyer, E., studies of the phosphates, 201.
—— the two isomeric dibromopropanes, 908.
Esbach, G., estimation of urea in urine, 1067.
Estcourt, C., analysis of the waters of Lake Thirlmere and the River Vyrnyw, 906.
—— desirability of fixing by analysis some standards of value for beer based on the qualities usually sold in large towns, 290.
Etard, A., oxidation of aromatic compounds, 320.
—— researches on the sulphates, 104, 593.
Etard. See also Cahours and Gal.
Etti, C., Malabar-kino and kinoïn, 159.
Eugling, W., composition of the colostrum of the cow, 815.
Eugling, W., and v. Klenze, Alpine dairy produce, 857.
Ewald, H., some coerulignone derivatives, 253.
Exherich. See Michler.
Exner, F., electrolysis of water: galvanic polarisation, 577.
—— galvanic polarisation of platinum in water, 578.
Eyndhoven, A. J. v., gaslighting, 85.
Ezweiler, researches on perbromination, 701.

F.

Fahlberg, C., liquid toluene sulphonic chloride and Beckurts' so-called toluenemetasulphonic acid, 804.
Fahlberg, C., and I. Remsen, oxidation of orthotoluenesulphamide, 628.
Farsky, F., salicylic acid as a preventive of house-fungus, 1080.
Fassbender, R., double salts of calcium sulphate, 203.
Fesca, M., mechanical analysis of soils, 673.
Ficinus, O., preparation of pure tartaric acid, 917.
Field. See Jackson.
Fileti, M., chemical nature of the essence of Laurocerasus and of bitter almonds, 719.
—— cinchonine, 655.
Fileti, M., and R. Piccini, decomposition of phenylethylamine hydrochloride, 922.
Finkener, R., estimation of phosphoric acid as ammonium phospho-molybdate, 275.
Fischer, E., hydrazine-compounds of the paraffin series, 450.

Fischer, E. and O., certain colouring matters of the rosaniline group, 236.
—— dyes of the rosaniline group, 787.
—— remarks on Doebner's communication on "malachite-green," 787.
—— triphenylmethane, 326.
—— triphenylmethane and rosaniline, 384.
Fischer, F., heating steam boilers, 1070.
—— iron smelting in the cupola furnace, 564.
—— utilisation of suint from wool, 86.
—— wearing out of steam boilers, 410.
Fischer, G., new colouring matter from orthamidophenol, 924.
Fischer, O., condensation-products of tertiary aromatic bases, 53.
Fischli, H., paratoluic and terephthalic acids, 638.
Fittica, F., nitrobenzoic acids, 150.
Fittig, R., constitution of tiglic and angelic acids, 456.
—— formation of unsaturated hydrocarbons from the addition-products of non-saturated acids, 376.
—— uric acid formula, 142.
Fittig, R., and F. Binder, addition-products of cinnamic acid, 378.
Fittig, R., and F. Gebhard, fluoranthene, a new hydrocarbon from coal-tar, 165.
Fittig, R., and W. F. Hillebrand, quinic acid, 159.
Fittig, R., and H. Lippmann, constitution of isodiphenic acid and fluoranthrene, 536.
Fittig, R., and H. Schmitz, diphenylenemethane, 164.
Fittig, R., and C. Wurster, atropic and isatropic acids, 379.
Fitz, A., fungoïd fermentation, 172.
—— schyzomycetic fermentation, 664.
Flavitzky, F., amyl compounds, 37.
—— dehydration of propylene-glycol, 136.
—— dextrogyrate terpene from the turpentine of *Pinus sylvestris*, 168.
—— hydration of terpenes, 726.
—— structure of terpenes, 167.
Flavitzky, F., and P. Kriloff, isopropylacetylene, 134.
Fleck, E., manufacture of artificial mother-of-pearl and of imitations of marble from glue, 996.
Fleitmann, T., preparation of malleable nickel and cobalt, and the application of these metals, 563.
Fletcher, J., preparation of sulphuretted hydrogen, 1013.
Flowers, H., lactucarium, 1041.
Fluegger, T., spitting of silver, 438.
Forcrand, organic ultramarines, 329.
Foudlakowsky, G., lactoglucose and galactose, 137.
Fouqué, F., and M. Lévy, production of felspars by fusion, and by prolonged maintenance at a temperature near that of fusion, 358.
Franchimont, N., zinc acetate, 452.
Franchimont, N., and Sicherer, the colouring matter of sandal and caliatour woods, 470.
Franchimont, N., and Wigman, betulin, 469.
—— —— lactucone, 468.
Fraude, G., aspidospermine, 470.
—— orthocresolphthaleïn, 634.
Freda, P., preparation of digallic acid, 645.
Fredericq, L., hæmocyanine from the blood of the *Octopus vulgaris*, 333.
Fremy, E., artificial formation of coal, 896.
Fresenius, R., alkaline constituents of the Hunyadi János springs at Buda-Pesth, 366.
—— estimation of the available zinc in zinc-dust, 400.
Freund, C., some galvanic properties of aqueous solutions of metallic salts, 863.
Freyberg, E., plant respiration, 736.
Friedel, Crafts, and Ador, durene derivatives, 713.
Friederici, T., action of hydrogen on metanitro - paratrichloraceto - toluide and metanitro - paravaleryl - toluide, 311.
—— new method of preparing chrysanisic acid, 324.
Friedländer, C., and E. Herter, action of carbonic acid on the animal organism, 174.
Fritzsche, P., oxyphenylacetic acid, 322.
Frommel. See Clermont.
Fuchs. See Cumenge.

G.

Gabba, L., and O. Textor, influence of the chemical composition of the water used in the preparation of raw silk, 493.
Gabriel, S., substituted phthalanils, 323.
Gabriel, S., and A. Michael, action of dehydrating substances on anhydrides, 245.
—— —— benzylmethylglycollic acid, 795.

Gabriel, S., and J. Zimmerman, dinitro-hydrocinnamic acid and its derivatives, 639.
Gail, F., oxidation of dioxydiphenylmethane, 325.
Gal, H., and A. Étard, researches on strychnine, 387.
Galimberti, A., a critical point in making Parmesan cheese, 764.
Gamgee, A., and E. Blankenhorn, protagon, 950.
Gatellier, E., absorption of atmospheric nitrogen by plants, 818.
Gaudin, M. A., application of the author's atomic theory to certain minerals, 602.
Gawalowski, a process for utilising the residue from the manufacture of potassium ferrocyanide, 680.
Gayon, V., inversion and alcoholic fermentation of cane-sugar, 336.
—— inactive glucose in crude cane-sugars, 97.
Gayon and Millardet, on the saccharine matter contained in vines suffering from phylloxera, 1048.
Gebhard. See Fittig.
Gerichten, E. v., β-chlorocymene from thymol, 230.
Gerichten, E. v., and W. Rössler, α-oxyparatoluic acid, 323.
Gerlach, G. T., extraction of sulphur by means of superheated steam, 284.
Gerland, W., and J. Roberts, preservation of beet-leaves and the preparation of brown hay from maize, 960.
Gernez, D., distillation of liquids under the influence of static electricity, 997.
Gerresheim, H., ammoniacal mercury compounds, 438.
Geuther, A., diethylglyoxylic ether and diethylglyoxylamide, 220.
Giacosa, P., action of amyl nitrite on blood, 816.
—— fermentation of hydroxyvaleric acid, 782.
—— phenolglycollic acid, 929.
Giacosa. See also Nencki.
Girard, A., conversion of hydrocellulose into pyroxylin, 911.
—— hydrocellulose, 779.
Girard and Pabst, nitrosyl-derivatives, 383.
Giraud, E., derivatives of indigotin, 936.
Gluge, O., calcium chloride, 562.
Göbel, W., purification of gas by ammonia, 986.
Götschmann, T., methyl- and dimethyldiacetonamine, 1035.
Goldberg, A., parahydroxysalicylic acid, 928.
Goldberg. See Schmitt.
Goldschmidt, A., the three isomeric tolidines, 235.
Goldschmidt, G., idrialin, 167.
Goldschmidt. See also Barth.
Goldstein, M., action of nitric acid on phenol and on nitrophenol, 148.
—— boiling points of normal ethanes (paraffins), 765.
—— dibenzoyl-dinitro-diphenol, 148.
Golubeff, P., action of nitric acid on deoxybenzoïn, 150.
—— nitro- and amido-derivatives of deoxybenzoïn, 790.
Gorgeu, A., artificial manganese dioxide, 600.
Gottfriedsen, on tanning and mineral tanning, 100.
Graebe, C., alizarin-blue, 259.
—— alizarinsulphonic acid, 655.
Graebe, C., and H. Bungener, synthesis of chrysene, 807.
—— —— synthesis of deoxybenzoïn, 790.
Graebe. See Caro.
Grätzel, A., eupittone and pittacal, 253.
Grandeau, L., influence of atmospheric electricity on plants, 818.
Grawitz, S., action of chromium salts in presence of chlorates, 420.
—— formation of aniline-black by chromate in presence of chlorates, 495.
Greene, H., preparation of hexamethylbenzene from acetone, 904.
Greene. See also Le Bel.
Greenish, H. G., *Bidara laut*, 1045.
Grenfell, J. G., supersaturated solutions, 501.
Grete, E. A., estimation of nitric acid as ammonia, 79.
—— estimation of nitrogen in nitrogenous organic bodies, 80.
—— formation of nitrites in the soil, 737.
Griess, P., action of cyanogen on amido-benzoic and anthranilic acids in aqueous solution, 321.
—— action of some diazosulphonic acids on phenols, 315.
—— amidobenzoic percyanide, 466.
—— derivatives of benzoic acid, 246.
—— remarks on Weselsky's and Benedikt's investigation on some azo-compounds, 629.
Grimaux, E., pseudouric acid, 784.
—— synthesis of uric acid derivatives, 460.
—— synthesis of uric acid derivatives: alloxan, uramil, murexide, &c., 375.

Grimaux, E., and J. Tscherniak, preparation of malonic acid, 782.
Grimshaw, H. and C., analysis of the water of Thirlmere, 211.
Grodzki. See Krämer.
Grosheintz, H., tetrallylammonium bromide and triallylamine, 779.
Grosjean, H., analysis of some fodders and observations on the damage caused to Italian beans by the bean insect, 552.
Grossman, J., softening magnesia-hard water, 985.
Grothe, O., metaiodonitro- and metaiodamido-benzoic acids, 377.
Gruber, M., action of nitrous anhydride on protocatechuic acid, 643.
Guareschi, J., ethylidenedisulphuric acid, 710.
Gümbell, C. W., phyllite or sericite-gneiss, 207.
—— the stone of the "Julius Column," the Lavez rock in the Upper Engadine, and the sericite-gneiss in the Bundener Alps, 25.
Guignet, E., constitution of coal, 602.
Guldberg and Waage, chemical affinity, 580.
Gunning, J. W., action of alcohol on bacteria, 817.
—— conditions of life of the lower organisms, 664.
—— ferric chloride as a purifier of water, 1072.
Gustavson, G., bromination of aromatic hydrocarbons in presence of aluminium bromide, 142.
—— compounds of aluminium chloride with benzene and toluene, 461.
—— compounds of cymene with aluminium bromide and chloride, 785.
—— interpretation of reactions occurring in presence of aluminium chloride, 785.
—— compounds of aluminium chloride with benzene and toluene, 308.
Guthrie, F., on salt solutions and attached water, 428.
Gutknecht, H., diagnosis of fatty alcohols, 673.
Guyard, A., action of oxalic acid on chlorates, bromates, and iodates, 593.
—— copper and ammonium oxyferrocyanides, 775.
—— iodated potassium iodide, 595.
—— Laurent's "Carminaphtha," 466.
—— law peculiar to metallic ferrocyanides, 830.
—— separation and estimation of chlorine, bromine, and iodine, 670.
—— viscosity, a cause of catalysis, 876.
Guyot, P., deposits of calcium phosphate in the Vosges, 19.

H.

Haas, B., ripening of grapes, 174.
Haberlandt, F., cohesive power of soils, 957.
—— evaporation of water from the ground, 667.
—— strength of hemp, 859.
Habermann, J., glycyrrhizin, 1040.
Haddan, H. J., treating ores containing silver and copper, 496.
Häusserman, C., manufacture of methylaniline, 995.
Hager, H., butter analysis, 81.
—— estimation of alcohol and extractive matter in wine, 179.
—— testing milk for starch powder, 674.
Hahn. See Staedel.
Haitinger, L., nitrobutylene, 700.
Haller, A., cyano-derivatives of camphor, 329.
—— iodo-camphor, 329.
Hanimann and Hanhart, desulphurisation of dithiodidimethylaniline, 714.
Hammarsten, O., paraglobulin, 472.
Hammerl, H., freezing mixture of calcium chloride and snow, 689.
—— solution of carbonic oxide in an acid solution of cuprous chloride, 887.
Hanhart, action of chloroform and perchloromethane on dimethylaniline, 714.
—— action of copper on trichlorobenzene, 714.
Hanhart. See also Hanimann.
Hanko, W., modification of Simpson's method for estimating nitrogen, 554.
Hanriot, derivatives of glycerol, 1029.
—— on glycide, 449.
Hansel, v., phosgenite from Monte Poni, Sardinia, 604.
Harnack, E., the basic constituent of Dita bark, 332.
Hartmann, M., basalts of the Auckland Islands, 903.
Hartwig, E., oil of wine, 615.
Harz, C. O., spergulin, a new fluorescent body, 469.
Hauer. See Müller.
Hawliczek. See Lippmann.
Head, dephosphorisation of pig iron, 1075.
Hecht, O., and J. Munier, isoheptylic acid from β-hexyl iodide, 140.

Heckel, E., influence of salicylic acid, thymol, and some essential oils on germination, 172.
Hehner, O., determination of phosphoric acid as phosphomolybdate, 482.
—— examination of Pavy's method of determining glucose, 834.
—— method of testing butter, 181.
—— the influence of chloroform on nitrification, 395.
Heiden, on the supply of nitrogen to plants, 739.
Heinrich, R., artificial manures, 1050.
—— estimation of dextrose and inverted sugar in presence of saccharose, 180.
Heintz, W., benzaldiacetonamine, 54.
—— vanillo-diacetonamine, 144.
Heinzelmann, R., dehydromucic acid, 141.
Heinzelmann and L. Spiegelberg, pentabromobenzene-sulphonic acid, 802.
Helkenberg. See Tiemann.
Hell, C., and O. Mühlhäuser, action of bromine on acetic acid, 705.
—— —— addition-product of acetic acid with bromine and hydrobromic acid, 705.
—— —— addition-product of acetic acid with bromine and hydrochloric acid, 705.
Hell, C., and P. Schoop, aniline residues, 715.
—— —— dibromocapric acid, 521.
Helm, O., gedanite, a new fossil resin, 300.
—— microscopical properties of amber, and the amount of sulphur contained in it, 300.
—— the sulphur in fossil resin, 896.
Hempel, W., estimation of hydrogen in gaseous mixtures, 670.
—— fractional combustion of hydrogen and marsh-gas, 747.
—— limit of detection of carbonic oxide, 1063.
—— simultaneous determination of carbon, hydrogen, and nitrogen in elementary analysis, 278.
Henneberg, W., determination of fibrin, 835.
Henneberg, W., E. Kern, and H. Wattenberg, fattening of sheep, 811.
Henrichsen, S., specific heat of water, 1002.
Henry, L., a new unsaturated hexavalent hydrocarbon, diallylene, C_6H_8, 34.
Hensgen, C., action of hydrochloric acid on double sulphates, 105.
—— action of hydrochloric acid gas on sulphates, 105.
Hensgen, C., new double salt of chromic acid, 887.
Hepp, some addition-products of trinitrobenzene and other nitro-compounds, 50.
Héraud, A., new voltaic element with constant current, 426.
Hering, C. A., recovery of antimony, 491.
Hermann, R., specific gravity and atomic volume of the cerium metals, 579.
Herter, E., tension of oxygen in arterial blood, 811.
Herter. See also Friedländer.
Herth, R., chemical nature of peptones, 660.
Hertz, J., estimation of silver, chlorine, bromine, and iodine by ammonium thiocyanide, 973.
Herwig, H., the quantity of electricity necessary for the complete charge of a platinum-water-cell and the distance between the molecules of liquid water, 194.
Herzig, J., two new isomerides of cyanuric acid, 517.
Hesse, H., refining copper, 9.
Hesse, O., Alstonia bark, 332.
—— amyrin and icacin, 73.
—— appendix to the estimation of carbonic acid in the air, 78.
—— behaviour of potassium thiocyanate with some of the quinine alkaloïds, 281.
—— cinchotenicine, 332.
—— conquinine sulphate, 656.
—— further remarks on *Alstonia constricta*, 269.
—— lotur bark, 73.
—— on asphalt and other retinalites, 301.
—— paricine and aricine, 1043.
—— remarks on cinchonine and cinchonidine, 71.
—— remarks on Rice's article on the cinchona alkaloïds, 71.
—— substitutes for quinine, 71.
—— test for quinidine, 281.
—— test for quinine, 280.
Hessert, J., phthalyl alcohol, 634.
Hétet, F., *Sarracenia purpurea*, 541.
Heumann, K., potassum ultramarine, 692.
—— silver ultramarine, 437.
Heyden, F. v., and T. Eckart, preservation of meat, 996.
Higgin, dibenzanilides, 716.
Hilger, A., chemical composition of the soils of the vine-growing districts of the Rhine and Maine, 737.
—— composition of "grains" from malt, 761.

Hilger, A., detection of ethyldiacetic acid in urine, 560.
—— mineral constituents of horse-radish, 819.
—— solanine and the products of its decomposition, 541.
Hilger, A., and Bischoff, H., colouring-matter of the Caryophyllaceæ, 730.
Hill, H. B., di-substitution-derivatives of acrylic acid, 616.
Hill. See also Bennett, Jackson, and Mabery.
Hille, poisoning of fowls with pumpkin seeds, 1046.
Hillebrand. See Fittig.
Hiortdahl, a new metal discovered by T. Dahll, 890.
—— crystalline form of the stannmethyl compounds and their homologues, 518.
Hiriakoff, M., examination of a meteorite found in the neighbourhood of Berdjansk, 445.
Hirsch, B., investigation of *Balsamum antarthriticum indicum*, 262.
Hirsch, R., the so-called dichlorazophenol, 315.
Hittorf, W., proof of the statement that "electrolytes are salts," a reply to L. Bleekrode, 1.
Holzner, G., researches on beer, 1079.
Hönig, M., and M. Rosenfeld, sugars, 449.
Hörmann, J. v., action of hydrocyanic acid on epichlorhydrin, 449.
Hörmann. See also Liebermann.
Hoffmann, E., maringin, 468.
Hoffmann, R., ultramarine, 108.
Hofmann, A. W., action of phosphorus pentachloride on thiocarbimides, 805.
—— angelylthiocarbimide, 712.
—— formation of methyl aldehyde, 219.
—— modified vapour-density determination, 196.
—— piperidine and piperine, 733.
Hofmeister, F., complete precipitation of albumin from animal fluids, 183.
—— regeneration of albumin from peptone, 950.
Holdermann, E., iron albuminates, 170.
—— on hydrochloric acid containing phosphoric acid, 8.
Holliday, J., improvements in dyeing and printing aniline black, 422.
Hollway, J., a new application of rapid oxidation by which sulphides are utilised for fuel, 755.
Hoogewerff, S., and W. A. van Dorp, oxidation of quinine, 946.
Hoogewerff, S., and W. A. van Dorp, oxidation of quinine by potassium permanganate, 541.
—— —— oxidation of quinoline, 731.
Hoppe-Seyler, F., lecithin and nuclein in beer-yeast, 811.
—— a simple experiment to show the evolution of oxygen by plants in sunlight, 819.
Horstmann, A., relative affinity of oxygen for carbonic oxide and hydrogen, Part II, 436.
Hübner, H., iodosalicylic acids, 928.
—— nitrosalicylic acids and the isomerism of benzene-derivatives, 380.
Hübner, H., S. M. Babcock, and H. Schaumann, nitrosalicylic acids and dinitrophenol, 928.
Hübner, H., and E. Simon, diethyl- and diamyl-anhydrobenzoyldiamidobenzene compounds, 923.
Hüfner, G., chemistry of the bile, 949.
—— estimation of hæmoglobin and oxygen in the blood, 835.
—— estimation of urea by means of sodium hypobromite, 405.
Hummel, J., diphenic acid, 165.
Hurter, F., estimation of cyanogen in soda-lyes, 402.
Husson, C., examination of coffee, tea, and chicory, 558.
Husson. See also Bancel.
Hutchinson, C. C., Schützenberger's process for the volumetric estimation of oxygen in water, 77.

I.

Iles, M. W., and I. Remsen, oxidation of sulphamido-xylene, 52.
Ilgen, O., Solvay's soda used in the preparation of ultramarine, 987.
Ireland, J., Blair's process for iron manufacture, 89.
Isambert, dissociation of ammonium hydrosulphide, 880.

J.

Jackson, C. L., and A. W. Field, parachlorobenzyl chloride and bromide, 62.
Jackson, O. R., and H. B. Hill, mucobromic acid, 224.
Jacobsen, O., constitution of oxymesitylenic acid, 248.
—— constitution of the propyl group in cymene, 228.

Jacobsen, O., hydroxyparaxylic acid, 641.
—— isocymene, 624.
—— oxidation of metaxylene-sulphamide, 53.
—— products of the action of fused potash on potassium mesitylenesulphonate, 529.
—— sulphaminemesitylenic acid and a new hydroxymesitylenic acid, 643.
Jacobsen, O., and E. Weinberg, dibromometaxylenesulphonic acid, 61.
Jaffe, M., acids produced by the introduction of chloro- and bromo-benzene into the animal system, 796.
—— synthetic processes in the animal body, 176.
Jagi, *Paeonia Moutan*, 306.
Jahn, H., valonia and certain other sources of tannin, 248.
Jaillard, absorbing power of wood charcoal, 761.
Jannasch, P., and C. Rump, discovery of vanillin in Siam benzoin, 245.
Jawein. See Beilstein.
Jenkins. See Johnson.
Jeremin, ozone, 8.
Joclet, V., use of chrome-alum instead of potassium dichromate in wool-dyeing, 185.
Johanson, E., chemical constituents of the willow, and its pathological formations: certain reactions with tannin and allied substances, 160.
Johnson, O., test for arsenic, 277.
Johnson, S. W., and E. H. Jenkins, determination of nitrogen in the analysis of agricultural products, 962.
—— —— determination of phosphoric acid, 966.
Johnstone, W., analysis of the water of St. Dunstan's well, Melrose, 905.
Jolly, L., distribution of phosphates in the blood, 662.
Jones, H. W., amount of ash and soluble matter in the three kinds of Buchu, 391.
Jonge, D. de, secretion from the sebaceous glands of birds, 176.
Jordan, P., preparation of manganiferous pig-iron, 755.
Jörgensen, S. M., cobalt-ammonium compounds, 119, 597.
Joulie, H., retrogradation of superphosphates, 987.
Jousselin, L., nitrosoguanidine, 613.
—— salts of guanidine, 914.
Jussieu, F. de, alloys of lead and antimony, 889.
Just, L., influence of temperature on the germination of seeds, 393.

K.

Kachler, J., Borneo camphor, 1039.
Kahlbaum, G. W. A., physical properties of some methyl compounds of 3- and 4-carbon acids, 521.
Kalkowsky, E., the granite-porphyry of Beucha near Leipzig, 27.
—— the leucitophyr of Lake Averno, 609.
Kallab's new bleaching process for animal textile fibres, 99.
Kaschirsky, M., action of zinc-methyl on the bromides of monobrominated acid radicles of the α-series, 46.
Katzujama, investigation of the seeds of *Camellia Japonica*, 330.
Keith's process for desilvering and refining raw lead by electrolysis, 288, 410.
Kelbe, W., hydrocarbon from rosin-oil, 467.
—— naphthyl phosphorus and arsenic compounds, 67.
Kellermann, C., composition of the growing potato, 174.
Kellner, O., nitrogenous constituents of young grass and hay, 829.
—— nutritive value of malt, 1049.
Kelly, O. J., action of chlorocarbonic ether on halogen-compounds of the fatty acid series, 305.
Kenngott, A., on unghwarite, nontronite, gramenite, &c., 31.
—— polydymite, 18.
—— the fundamental forms of crystal species, 14.
Kern, S., action of sea-water on iron and steel plates, 564.
—— distribution of manganese in ferromanganese alloys, 286.
—— manganese steel, 567.
—— preparation of chrome crucible steel, 567.
—— purification of cast-iron from phosphorus, 286.
—— steel making, 567.
—— working of mild steel, 410.
Kernlter, F., on making red wine, 681.
Kessel, F., bromo-derivatives of ethyl acetate, 137.
—— decomposition of ethyl monobrom- and dibrom-acetate, 220.
—— double salts of cuprous thiosulphate, 124.
—— wax of *Ficus gummiflua*, 261.
—— atomic weight of antimony, 772.
—— estimation of manganese, especially in its alloys with iron, 341.
—— law of multiple proportions, 691.
Killing, K., the gneiss of the North

Eastern Schwartzwald and its relationship to the mineral veins, 443.
Kinnicutt. See Anschütz.
Kirchner, W. J., and Du Roi, beet leaves as fodder for cows, 813.
Kirmis, M., transference of the ions, 193.
Kjedal, J., rotatory power of beer worts, 993.
Kleemann, spent hops as fodder, 1050.
Klein, L., estimation of carbon in cast-iron, 401.
Klein, O., compounds of organic bases with mercuric chloride, 231.
Klein, P., diaspore from Jordansmühl, 603.
—— manganosite from Langban, Sweden, 605.
Klein. See also Pinner.
Kleinschmidt. See Staedel.
Kleuze. See Eugling.
Klien, chromium garnet in Silesia, 361.
—— catlinite, 361.
—— fluorite from Evigtok in Greenland, 511.
Klinger. See Bernthsen.
Klipstein, v., the nepheline rock of Meiches in the Odenwald, 607.
Klocke, F., the "etch figures" produced on the alums, 439.
Knoch. See Otto.
Knop, W., diabase from Berneck, 443.
—— the greenstone soil of Berneck, 824.
Knott. See Otto.
Koch, A., adular from Verespatak, 359.
—— colouring matter containing sulphur derived from dimethylparaphenylenediamine, 628.
—— pseudobrookite and szaboite, new minerals, 441.
Koch, K. R., changes in the surface of platinum and palladium produced by oxygen-polarisation, 1005.
Koch, method of photographing bacteria, 1046.
Köbig, J., constituents of Roman chamomile oil, 454.
Köhler, H., action of ammonium sulphate on barium ethylsulphate, 137.
—— decomposition of ethylsulphates by gaseous hydrochloric acid, 137.
—— ethereal oils of some Ericaceæ, 641.
—— formation of ethylamine, 219.
—— mercuric chloride, 1017.
—— mercuric iodide, 602, 889.
—— substituted nitrogen chlorides, 780.
Koenig, G., ankerite from Phœnixville, 604.
—— simultaneous occurrence of grossular, zoisite, stilbite, and leidyite, 606.
König, D., decomposition of bones by steam, 987.
König, G. A., chromometry, an application of the blowpipe to quantitative analysis, 740.
König, H., action of hydrocyanic and hydrochloric acids on ethyl methylacetoacetate, 706.
Koenigs, W., action of fuming nitric acid and of nitrous acid on benzenesulphuric acid, 314.
—— nitrochinoline, 540.
—— oxidation of cinchonine quinoline by potassium permanganate, 731.
—— oxidation-products of cinchonine, 471.
—— synthesis of chinoline from allylaniline, 540.
Köppen, E. v., physical and chemical changes which specular iron undergoes, when smelted in the cupola furnace, 840.
Körner, H., paradipropylbenzene and its derivatives, 142.
Koettstorfer, J., new method for detecting foreign fats in butter, 983, 1069.
Kohn, S., decomposition-products of albuminoïds, 389.
Konigel-Weisberg, J., action of chlorine on barium hydrate, 505.
—— action of chlorine on strontia, 596.
Kopp, H., acids obtained by the saponification of Roman chamomile-oil, 454.
—— determination of atomic weights and the use of isomorphism for the same, 769.
Korschelt, saki, the alcoholic drink of the Japanese, 413.
Kossel, A., chemical composition of peptones, 811.
Krämer, G., and M. Grodzki, the acids of wood vinegar and their connection with the so-called wood oils, 43.
Krafft, F., conversion of undecylenic acid into undecylic acid, 306.
Krandauer, analysis of waters for brewing, 1078.
Krandauer. See also Lintner.
Krauch. See Mutschler.
Krause, A., paraphenylenediamine, 462.
Krause, H., and G. Salomon, formation of xanthine derivatives from albumin, 471.
Kraut, K., mercuric iodide, 772.
Kressner. See Dietzell.
Kriloff. See Flavitzky.
Kühnemann, G., constituents of hops, 171.
Kurbatow. See Beilstein.

L.

Labhardt, E., nitration of bromonaphthalene, 721.
Lachmann, G., tolylthiocarbimide, 935.
La Coste, W., and A. Michaelis, mono- and di-phenyl compounds of arsenic, 161.
—— —— monotolyl compounds of arsenic, 163.
—— —— triphenylarsine and its derivatives, 162.
Ladenburg, A., artificial atropine, 733.
—— derivatives of tropic acid, 720.
—— di-isobutylamine, 703.
—— experimental determination of position, 232.
—— simple method for preparing aldehydines, 233.
—— tropidine, 733.
Ladenburg, A., and T. Engelbrecht, some phenylaldehydines, 234.
Ladenburg, A., and L. Rügheimer, orthotolylenediamine derivatives, 715.
—— —— the aldehydines, 233.
Ladureau, A., influence of the time of manuring in the beet cultivation, 825.
—— nitrates in sugar beets, 826.
Lagermark, G., synthesis of tetrolic acid, 782.
Lagermark, G., and A. Eltekoff, action of sulphuric acid on acetylene, 780.
Laiblin, R., nicotine and nicotinic acid, 808.
Lamansky, S., Stokes's law, 862.
Land, O., garnet from the erratic gneiss of Wellen, near Bremen, 361.
Landauer, J., absorption spectra, 101.
Landgrebe, O., cyanoguanidine, 53.
—— oxidation of ditolylparabanic acid, 62.
Landolph, F. H., action of boron fluoride on acetone, 914.
Landshoff. See Tiemann.
Lang, C., heat-capacity of soils, 958.
Langbein, G., South American saltpetre, 1073.
Lange, A., diphenylthiohydantoïn, 651.
Lapper. See Bell.
Lasaulx, A. v., an intergrowth of two micas from Middletown, Connecticut, 363.
—— crystal system of tridymite, 358.
—— iodobromite, a new silver haloïd, 365.
—— optical properties and crystal form of tridymite, 605.
—— saccharite, 360.
Lasaulx, H. v., breislakite, 206.
Latschinoff, P., oxidation of cholic acid, 810.
—— some neutral oxidation-products of cholesterin, 135.
Laufer, E., behaviour of quartz with microcosmic salt, 79.
Laugier, E., analysis of raw sugars, 404.
—— determination of free acids in oils, 406.
Lauterbach, P., nitration of derivatives of the paraffins, 700.
Lavender, R., improvements in treating waste sulphuric acid that has been used for pickling iron plates, and other articles of iron or steel, 423.
Lawrence, R., and C. W. Reilly, analysis of Burton ales and Dublin porter, 344.
Lebaigue, E., apparatus for continual dialysis, 347.
Le Bel, J. A., dextrogyrate amyl alcohol, 369.
—— limit of the separation of alcohol from water, 703.
—— methylpropyl carbinol prepared by synthesis, 1029.
Le Bel and Greene, action of zinc chloride on methyl alcohol; hexmethylbenzene, 49.
—— —— action of zinc chloride on normal butyl alcohol, 1029.
Lechartier, G., action of potassium pyrogallol on nitric oxide, 1012.
—— estimation of organic matter in natural waters, 976.
—— preservation of green fodder in pits, 1049.
Le Chatelier. See Mallard.
Lecher, E., heat capacity of mixtures of methyl alcohol and water, 688.
Leclanché, an improvement of the peroxide of manganese battery, 1.
Leclerc, A., nutritive value of seed-bearing beet-root, 822.
Leeds, A. R., action of potassium permanganate on oxalic acid, 353.
—— alteration of standard ammonium chloride solution when kept in the dark, 400.
—— ammonium nitrate and the bye-products obtained in the ozonisation of air by moist phosphorus, 881.
—— detection and estimation of nitrous acid in potable waters, acids, &c., 964.
—— estimation of nitrates in very dilute solution, 1062.
Lefort, J., tritungstates, 600.
—— tungstates of the earthy and metallic sesquioxides, 355.
Lehmann, A., constitution of ultramarine, 204.

Lenz, W., fluorbenzenesulphonic acid and the melting points of substituted benzenesulphonic acids, 649.
Lepel, B. F. v., new universal stand for use with the pocket spectroscope, 574.
Lepel, F. v., adulteration of wine, 82.
Lescœur, H., and A. Rigaut, solid cyanogen hydride, 1028.
Letts, E. A., some bismuth residues, 355.
Lévy. See Fouqué.
Lewin, L., spongy iron and animal charcoal as materials for purifying water, 343.
Lewis. See Storer.
L'Hote, L., process for enriching phosphates containing earthy carbonates, 490.
Lieben, A., density of chlorine at high temperatures, 1011.
Lieben, A., and L. Zeisel, croton aldehyde and its homologues, 615.
Liebermann, C., anthracene derivatives of the chrysazin series, 537.
—— reduction of anthraquinone-sulphonic acids, 537.
—— synthesis of anthrarufin and chrysazin from anthracene, 260.
Liebermann, C., and K. Boeck, anthracene-disulphonic acid and its conversion into anthrarufin, 257.
Liebermann, C., and J. Dehust, constitution of anthrarufin and oxyanthrarufin, 942.
Liebermann, C., and S. Hamburger, formulæ of quercitrin and quercetin, 944.
Liebermann, C., and O. Hörmann, anthrol, 653.
—— —— formulæ of rhamnetin and xanthorhamnin, 271.
—— —— glucoside of buckthornberries and rhamnodulcite, 39.
Liebermann, C., and P. Seidler, chrysarobin in "Goa powder," 326.
Liebermann, L., gas evolved by the action of barium hydrate on albuminoïds, 735.
Liebisch, T., mineralogical-petrographical notes on the granite-porphyry of Lower Silesia, 29.
—— occurrence of disthene in Central Africa, 24.
—— some syenite-porphyries of South-west Norway, 362.
Liebscher, Briem, and R. Burger, exhaustion of the soil by beet-root cultivation, 1050.
Lindo, D., analysis of caoutchouc, 559.
Link, A., and R. Mocket, on the delicacy of some reactions for hydrocyanic acid, 403.
Linnossier. See Chapuis.
Lintner, C., Krandauer, and Treiber, effect of artificially manured barley on the composition of the wort, 959.
Lippmann, E., and J. Hawliczek, eikosylene, a derivative of lignite paraffin, 447.
—— —— eikosylene, a derivative of brown-coal paraffin, 699.
Lippmann, E., and W. Strecker, amylidene-aniline, 462, 714.
—— —— nitrocuminol and its derivatives, 464.
Lippmann, E., and G. Vortmann, compounds of cobalt and nickel chlorides with anilines, 461.
Lippmann. See also Fittig.
List, K., magnetic compounds having the formula $RO.Fe_2O_3$, 13.
Livache, A., abnormal solubility of certain bodies in soaps and alkaline resinates, 99.
Lockyer, J. N., recent researches in solar chemistry, 425.
—— researches on spectra, 575.
Lösecke, A. v., formation of ammonium nitrate, 298.
Lösekann, G., action of sulphuretted hydrogen on alkaline solutions of alumina, 437.
Loew, O., detection of lecithin, 835.
—— oxidation of albumin by the oxygen of the air, 389.
—— source of hippuric acid in the urine of herbivorous animals, 952.
Löwig, G. and F., preparation of alkaline aluminates, 491.
—— —— preparation of alumina, 490.
Loir, chemical functions of acetic anhydride, 621.
Long, H., action of alcoholic potash on bromoform, 126.
Longuinine, W., thermic effect of substitutions, 871.
Lorenz. See Sonntag.
Lorin, M., preliminary study of the action of acids on salts without the intervention of a solvent, 689.
Losanitch, S. M., action of potash on tetranitrodiphenyl carbamide, 67.
Luca, S. de, a thread-like substance found in the excavations of Pompeii, 680.
—— presence of lithium in the earths and water of the Solfatara at Pozzouli, 33.
—— splitting up of cyclamin into glucose and mannite, 70.
Lübawin, N., nucleïn from cows' milk, 735.
Luginin, W., influence of substitution

on the evolution of heat during formation of salts, 767.
Lugwig, E., milarite, 358.
Lunge, G., antichlor, 676.
—— application of Witt's tropæoline to titration, 176.
—— behaviour of the nitrogen acids with sulphuric acid, 770.
—— estimation of nitrous and nitric acids, 79.
—— existence of nitrous anhydride in the gaseous state, 502.
—— preparation of nitrous acid, 200.
—— resin-sizing of paper, 994.
—— soda industry, 677, 751.
—— the amount of sulphuric acid in wines, 762.

M.

Mabery, C. J., and H. B. Hill, dimethyluric acid, 48.
Macadam, W. I., composition of a nodule of ozokerite found at Kinghorn-ness, 1020.
Macagno, J., action of the ferment of sour wine on good wine, 817.
Mach, E., experiments of the fining of wine, 1078.
Mactear, J., improvements in the manufacture of soda and potash, 422.
—— loss of nitre in the vitriol manufacture, 838.
Mader, C., apple and pear wine, 1078.
Maercker, M., gravimetric estimation of dextrose by means of an alkaline copper solution, 180.
Magatti, G., action of sulphuric anhydride on phenylthiocarbimide, 312.
Maillot, E., aniline-derivatives of sebacic acid, 376.
Mallard, E., bravasite, a new mineral, 442.
Mallard and Le Chatelier, detection of marsh-gas in the air of mines, 673.
Mallet, J. W., barcenite, a new antimonate from Huitzuco, Mexico, 1022.
—— nitrogen iodide, 882.
Maly, R., nitrosothiohydantoïn, 712.
Mandelin, A. F., quinine citrate, 1043.
Manetti, L., and G. Musso, composition of skimmed whey, 856.
Mann, C., new volumetric method for estimating zinc, 1054.
Manoury. See Steffens.
Marcano, V., and A. Muntz, utilisation of the banana, 568.
Marchand, E., milk from cows of different races, 749.
Marignac, C., on the discovery of a new earth announced by J. L. Smith, 12.
—— the gadolinite earths, 113.
—— ytterbium, a new metal from gadolinite, 118.
Markl, A., artificial yeast for molasses distilleries, 1078.
Martin, G., a Japanese cinnamon bark, 320.
—— constituents of *Ligustrum Ibotu*, 330.
—— *Evodia glauca*, 333.
—— *Scopotia japonica*, 333.
Maskelyne, N. S., artificial diopside formed in a Bessemer converter, 513.
—— enstatite from South Africa, 513.
Massenbach, V., experiments with artificial manures, 958, 1050.
Mateyczek. See Steffens.
Matthey, F., decomposition of lead sulphate by sodium chloride, 124.
Matthey, G., preparation of iridio-platinum, 772.
Maumené, E., composition of slate, 1024.
Mauro, F., the spinelle of Tiriolo, in Calabria, 694.
Mazzara. See Paternò.
Medicus, L., and E. Schwal, estimation of starch in sausages, 979.
Méhu, C., estimation of urea, 985.
—— Marchand's method of determining the butter in milk, 675.
Meldola, R., a cause for the appearance of bright lines in the solar spectrum, 574.
—— naphthalene derivatives, 165.
Melikoff. See Werigo.
Menke, A. E., reactions of iodine and of potassium iodide with sulphurous acid, 352.
Menozzi. See Murro.
Menschutkin, N., etherification of primary alcohols, 36.
—— etherification of secondary alcohols, 214.
—— etherification of tertiary alcohols and phenols, 215.
Merz, V., and W. Weith, action of bromine on the higher paraffins, 302.
—— —— action of bromine on the lower paraffins, 302.
Merz., V., and G. Zetter, preparation of trinitroresorcinol and trinitroorcinol, 717.
Merz. See also Diehl.
Meulen (B. van der). A new copper nitrite, 693.
Meunier, S., artificial production of native carburetted iron, 693.

Meunier, S., metallic granules of sporadosidereal meteorites, 609.
Meyer, A., absorption-spectra of solutions of brucine, morphine, strychnine, veratrine, and santonine in concentrated acids, 269.
Meyer, C. and V., vapour-densities of some inorganic bodies, 579.
Meyer, E. v., some new platinum compounds : fulminoplatinums, 373.
Meyer, F., preparation of large regular crystals, 352.
Meyer, G., action of carbonic anhydride on certain cyanides, 303.
Meyer, L., purification of mercury, 602.
Meyer, O., the rock of the St. Gothard tunnel, 366.
—— twin zircon crystals, 363.
Meyer, R., derivatives of hydroxypropylbenzoic acid, 795.
—— hydroxylation by direct oxidation, 139.
—— the mineral spring of "Tenniger Bad," Somvaaer, Tobel, Grisons, 33.
Meyer, R., and J. Rosicki, hydroxypropylbenzoic acid, 157, 465.
Meyer, V., determination of vapour-density, 177.
—— occurrence of furfurol in glacial acetic acid, 137.
Meyer, V. and C., determination of vapour-densities of substances which attack mercury, or which boil above 440°, 294.
—— —— vapour-densities of some inorganic compounds, 875.
—— vapour-densities of some metallic chlorides, 1013.
—— vapour-density determinations of inorganic bodies at high temperatures, 766.
Michael, A., synthesis of phenol glucoside and of orthoformyl glucoside or helicin, 1038.
Michael. See also Gabriel.
Michaelis, A., a homologue of phosphenyl chloride, 721.
Michaelis, A., and F. Dittler, reactions of phenylphosphine, 528.
Michaelis. See also La Coste.
Michler, W., and G. Blattner, nitration of benzenesulphanilide, 922.
Michler, W., and E. Exherich, polysubstituted carbamides, 934.
Michler, W., and G. Moro, action of sulphochlorides on amines, 920.
Michler, W., and R. Zimmermann, polysubstituted carbamides, 935.
Mikosch, C., origin of chlorophyll granules, 174.
Millardet. See Gayon.
Miller, H. v., malonic acid, 917.
Miller, W. v., angelic acids of different origin, 45.
—— dimethacrylic acid, 307.
Millot, A., insoluble phosphoric acid in superphosphate, 1052.
Mills, E. J., researches in thermometry, 588.
Mills, E. J., and J. J. Smith, researches on chemical equivalents, 876.
Miquel, P., a new organised ferment, 817.
—— presence of an alcoholic ferment in the air, 394.
—— the succinic fermentation, 394.
Mitscherlich, on new phenomena shown by gases, 587.
Mittenzwey. See Schmitt.
Mockel. See Link.
Möe. See Zetter.
Möhlau, R., orthodiamidodiphenethole, 939.
Möhlau. See also Schmitt.
Moeller, J., fibrous materials, 859.
Mörner, K. A. H., alkali-albuminate and syntonin, 489.
Mohr, F., material for standard weights and measures, 102.
—— nature of cohesion and its chemical signification, 579.
Moissan, H., amalgams of chromium, iron, manganese, nickel, and cobalt, 693.
—— iron reduced by hydrogen, 887.
Moitessier. See Engel.
Monnet, F., F. Reverdin, and E. Nölting, influence of metatoluidine in the preparation of rosaniline, 625.
—— —— methylated derivatives of aniline and toluidine, and the colour obtained therefrom, 310.
—— —— presence of metanitrotoluene in commercial nitrotoluene, 625.
Montgolfier, J. de, derivatives of terebenthene, 328.
—— isomeride of borneol, 944.
—— terebenthene dihydrochloride, 944.
—— transformation of camphic acid into camphor, 726.
Moore, G. E., hetaerolite, a new mineral, 17,
Morawski, T., citramalic acid, 707.
Morawski, T., and J. Stingl, modification of Bunsen's method of manganese determination, 278.
—— —— potassium permanganate and its oxidation-products, 204.
—— —— volumetric estimation of manganese, 277.
Morawski. See also Stingl.
Morgan, T. M., composition of a well-water at Grouville, 1072.

Morley. See Claisen.
Moro. See Michler.
Morton, H., chronology of the isomeric purpurins, 943.
Moser, J., cultivation and preservation of maize, 960.
—— cultivation of dhurra or sorgho grass, 823.
—— potassium salts as a manure, 826.
Mott, H. A., American baking powders and alum, 107.
Motten, action of heat on sugar and sugar solutions, 911.
Mrowec, S., carbon bisulphide manufacture in Swoszowice, and its use for the extraction of sulphur, 837.
Mühlhäuser. See Hell.
Müller, F. C. G., gases in iron and steel, 437.
—— the Bessemer process, 566.
Müller, H., and C. Pauly, preparation of potassium nitrite, 595.
Müller, P., and Hauer, remarks on beer fermentation, 1079.
Müller-Jacobs, A., mordant for Turkey-red dyeing, 187.
Müntz, A., ripening of rye, 337.
Mulder, E., synthesis of dimethylbarbituric acid, 618.
Mulder, E., and G. J. W. Bremer, action of chlorine monoxide on ethylene, 303.
Muller, F. H. S., and F. Wiesinger, preparation of sulpho-compounds from diazo-compounds, 933.
Munier. See Hecht.
Muntz. See Marcano.
Murro, G., and A. Menozzi, formation of fat from caseïn in the ripening of cheese, 996.
Musculus, F., modifications of the physical properties of starch, 518.
Musculus, F., and J. de Mering, action of diastase, saliva, and pancreatic juice on starch and glucose, 370.
Musso. See Manetti.
Mustapha, I., active principle of *Ammi visnaya*, 1040.
Mutschler, L., and C. Krauch, composition of candle nut, 957.

N.

Narr, F., behaviour of electric currents in rarefied gases, 345.
Naumann, A., density and decomposition of nitric acid, 195.
—— dissociation of chloral hydrate, 690.
Nencki, M., relation of oxygen to the life of the microzoa, 953.
Nencki, M., and P. Giacosa, existence of bacteria or their germs in the healthy organs of animals, 1046.
Nencki, M., and F. Schaffer, action of chloral hydrate on ammonium thiocyanate, 306.
Nencki, M., and N. Sieber, new synthesis of glycocyamine, 70.
Nessler, J., pressing of red wine, 681.
—— detection of free tartaric acid, and of sulphuric acid, in wine, 981.
Neubauer, C., detection of wines adulterated with grape-sugar, 82.
Neubauer, C., and E. Borgmann, estimation of glycerin in wine, 404.
Newlands. See Duncan.
Niederist, G., action of water on the haloïd compounds of alcohol-radicles, 700.
Nietzki, R., derivatives of quinol (hydroquinone), 464.
Nikolsky. See Saytzeff.
Nilson, L. F., criticism on Bunsen's older method for separating arsenic from antimony, 1058.
—— scandium, 601.
—— ytterbia, 601.
Noble and Abel, combustion of gunpowder, 992.
Nölting. See Monnet.
Nordenskiöld, A. E., a new species of mineral, thaumasite, 21.
—— mineralogical notes, 364.
—— some minerals from Laangban, 21.

O.

Odermatt, W., formation of phenol from putrefying albuminoïd matters, 1037.
Ogier, J., liquefaction of silicium hydride, 436.
—— measurement of the heat developed in the formation of hydrogen phosphides and arsenides, 5.
—— thermic formation of silicon hydride, 767.
—— thermic researches on silicic ether, 767.
Oglialoro, A., characteristic reactions of picrotoxin and of some of its derivatives, 748.
—— phenylcinnamic acid, 640.
—— preliminary notice on *Teucrium fruticans*, 728.
Oglialoro. See also Paternò.
Orth, A., constancy and variation in the composition of the soil, 666.

Ost, H., pyromeconic acid, 307, 708.
Ostwald, W., chemical affinity, 348.
Ott, A., heliographic printing, 750.
—— on the preparation of paper for pigment or carbon photography, 560.
—— photolithography, 836.
Otto, R., constitution of sulphotoluide, 926.
—— preparation of sulphuretted hydrogen for chemico-legal investigations, 671.
—— sulphonic acids derived from sulphones, 649.
Otto, R., and O. Knoch, competitive cultivation of grass seeds, 824.
Otto, R., and A. Knott, action of sulphuric monochloride on sulphobenzide, 243.
Otto. See also Beckurts and Pauley.
Oudemans, A. C., quinamine, 1044.

P.

Paalzow, A., the oxygen spectrum and luminous appearances of rarefied gases in tubes with liquid electrodes, 861.
Pabst. See Girard.
Pagenstecher, A., angelic and tiglic acids, 455.
Pagliani, S., naphthylcarbamides, 723.
—— reaction of salicylic acid with ferric salts, 748.
Paijkull, S. R., mineralogical notices, 31.
Palmer. See Richards.
Panebianco, R., dimorphism of 1 : 4 acetotoluide, 626.
Patera, A., obtaining vanadium from the uranium ore of Joachimsthal, 989.
Paternò, E., constitution of cumic compounds and of cymene, 308.
—— propylbenzoic acid, 321.
Paternò, E., and G. Mazzara, benzylated cresol, 314.
—— —— cumolcarbonic acid, 642.
—— —— thermal water of Termini Imerese, 698.
Paternò, E., and A. Oglialoro, picrotoxin, 729.
—— —— supposed identity of columbin and limonin, 730.
Pauley, C., and R. Otto, decomposition of ethyl disulphoxide by potash, 219.
—— —— disulphoxides of benzene and toluene, 243.
Pauly. See Müller.
Pavy, F. W., volumetric estimation of sugar, 557.
Pawlow, D., tetramethylethylene and its derivatives, 536.
Pebal, L., action of hypochlorous acid on ethylene, 446.
Pechiney, A. R., preparation of anhydrous sodium sulphate from Glauber salt, 596.
Peckham, S. F., composition of the ashes of wheat bran, 961.
—— determination of specific gravities, 498.
—— explosion of the flour mills at Minneapolis, Minnesota, 1079.
Pedersen, R., influence of temperature on the evolution of carbonic anhydride by barley seeds, 1048.
Peirce, B. O., the electromotive power of gas elements, 998.
Pellet, H. P., ratio of the sugar in the beet to the phosphoric acid in the root and leaves, 818.
Penfield, S. L., chemical composition of triphylite, 695.
—— volumetric estimation of fluorine, 829.
Penney, M. D., alum in flour and bread, 556.
Perger, v., derivatives of anthraquinone, 253.
—— α-diamidoanthraquinone, 724.
Perkins, F. P., analysis of butter fat, 1070.
Perry, N. W., platinum-alloy assay, 555.
Petermann, A., carrot seed, 822.
Petit, A., a new alkaloïd, 658.
Petri, R., chondrin, 661.
Petri, J., detection of blighted wheat in flour by the spectroscope, 977.
Petri, C., fumaric and maleic acids, 372.
Pfaundler, L., vapour-density determinations at high temperatures of substances which attack mercury, 499.
Pfeiffer, E., estimation of nitric acid by potassium dichromate, 399.
—— oxalic acid not poisonous, 335.
—— separation of the alkaline earths from the alkalis, 341.
—— tetrathionic and pentathionic acids, 1013.
Philipp, G. H., green and blue ultramarine, 108.
Phipson, T. L., colouring matter of *Palmella cruenta*, 1042.
—— water from the river Dart, 906.
Picard, P., albuminoïd compounds of the organs, and of the spleen in particular, 175.
—— Bernard's method for the estimation of glucose in blood, 674.

Picard, P., researches on the urea contained in the organs, 175.
Piccard, J., cantharic acid and a hydrocarbon, C_8H_{12}, 270.
—— derivatives of cantharadin and their relation to the ortho-series, 655.
Piccini. See Fileti.
Pichard, alkaline reaction of free, mixed, and combined magnesium carbonates and silicates, 298.
Pickering, S., ammonium nitrate, 200.
Pictet, R., study of the molecular constitution of liquids by means of their coefficient of dilatation, specific heat, and atomic weight, 875.
Pierre, J., oiling of corn, 822.
Pierre, J., and E. Puchot, products of distillation of alcohols, 612.
Pillitz, W., analysis of the Zsadányer meteorite, 397.
Pilter, T., artificial animal charcoal, 844.
—— decomposition of phosphatic minerals, 839.
Pinner, A., and F. Klein, butylchloral hydrocyanide, 41.
—— —— conversion of nitriles into imides, 46.
—— —— imido-thio-ethers, 147.
Pirath. See Wallach.
Pisani, F., double selenides of lead and copper, 440.
—— wagnerite from Bamle, in Norway: Russian retinite, 441.
Planta-Reichenau, A. v., the mineral springs of Passugg, Solis, and Tiefenkasten, in the Grisons, Switzerland, 126.
Playfair, D., note on the detection of some rare metals in pyrites flue dust, 973.
Plugge, P., decomposition of mercuric cyanide by dilute acids alone and in presence of sodium chloride, 1064.
Pohl, J. J., a method of detecting the difference between natural and artificial turquoise, 209.
Poincaré, L., danger of employing methyl alcohol in certain industries, 335.
Pokorny, F., purification of beet-root syrup, 844.
Poleck and Biefel, quantitative determination of sulphur in illuminating gas, 78.
Pollacci, E., plastering of wine, 681, 762.
Ponomareff, J., allantoxanic acid, 226.
—— compounds of the uric acid group, 461.
—— some derivatives of allantoïn, 228.
Popper, R., quantitative determination of precipitates without filtering, washing, and drying, 480.
Portele, R., influence of heat on the ripening of grapes, 1047.
Porro, B., composition of grapes at different stages of ripeness, 820.
Porver, F. B., mineral water of Rosheim, in Alsace, 698.
Posen, E., amidohydro-cinnamic acid (phenylamido-propionic acid), 378.
Potilitzin, A., action of chlorine on anhydrous metallic bromides, 770.
—— action of selenium on metallic sulphides, 771.
Pott, R., researches on the chemical changes in the fowl's egg during incubation, 474.
Praetorius, H., nitration of benzophenone, benzhydrol, and diphenylmethane, 319.
Prætorius-Seidler, G., reactions of cyanamide, 910.
Precht, H., composition of the combustible gases in the Stassfurt potash mines, 603.
—— volumetric estimation of magnesium, 1053.
Preis, K., and B. Raymann, action of iodine on aromatic compounds with long side-chains, 623.
—— —— cholesterin, 634.
Preuse. See Baumann.
Price, A. P., improvement in the preparation and treatment of saccharine substances and compounds, 423.
Procter, H. R., determination of free acid in tar liquors, 980.
—— explosive product of solution of phosphorus in carbon bisulphide, 996.
—— Weselsky's reaction for phloroglucin, 979.
Prunier, L., hydrocarbons from American petroleum, 447.
—— quercite, 239.
—— solubility of cinchonine and estimation of cinchona barks, 489.
—— unsaturated hydrocarbons from the decomposition of American petroleum, 1025.
Prunier, L., and R. David, crystalline products obtained from Pennsylvanian petroleum, 309.
Puchot. See Pierre.
Pusch, Böhr's colorimetric process for the examination of drinking water, 553.
Puschl, C., sketch of the actinic theory of heat, 687.

Q.

Quincke, G., formation of emulsion and the influence of the bile on digestion, 549.

R.

Rabuteau, L., alcohols in potato fusel oil, 36.
Raepper, W. T., on a pseudomorph after anorthite, from Franklin, New Jersey, 1022.
Raetz, T., enamel for cast- and wrought-iron, 755.
Ramdohr, L., superheated steam, 838.
Ramme, G., phosphorus sulphides, 691, 883.
Rammelsberg, C., behaviour of silicates containing fluorine, especially topaz and mica, at high temperatures, 772.
—— determination of lithium, 830.
Rampe, H., poison for field mice, 1051.
Ramsay, W., on picoline and its derivatives, 262.
Raoult, F. M., vapour-tension and solidifying point of saline solutions, 4.
Rath, G. v., crystals of amazon-stone (microline) from Pikes Peak, Colorado, 515.
Rathke, B., action of phenyl-thiocarbimide on diphenylguanidine, 804.
—— aromatic thiocarbamides, 804.
—— diguanidine, 781.
—— phenylthiocarbamic acid, 54.
—— sulphuretted dicyanodiamine, 41.
Rauff, H., chemical composition of nepheline, cancrinite, and microsommite, 606.
Raymann. See Preis.
Reboul, diallyl-acetic acid, 372.
—— ethylidene chlorobromide, 369.
—— isomerism in the propyl series, 127.
Reichenberg, V., heat-absorption attending the solution of potassium chloride in water, 588.
Regnauld, J., chloroform as an anæsthetic, 747.
Reichardt, E., a boron mineral from Chili, 19.
—— analysis of the water of the mineral spring at Suhl, 516.
—— detection of chloroform, 280.
—— distribution of fungus, 479.
—— uran-pecherz from Joachimsthal, 18.
Reichert, E., simplification of Hehner's method of testing butter, 406.
Reilly. See Lawrence.
Reimann, M., chrome-black on wool, 572.
—— valuation of body colours, 179.
Reimer. See Tiemann.
Reiset, J., the proportion of carbonic anhydride in the air, 744.
Remsen, I., oxidation of xylene-sulphamides, 248.
Remsen. See also Fahlberg and Iles.
Renouard, A., analysis of silk cocoons, 952.
Renoul. See Urbain.
Reverdin. See Monnet.
Reynolds, J. E., sugar as a test of the purity of water, 1062.
Riban, J., compounds of hydrogen phosphide with cuprous chloride, and its estimation in gaseous mixtures, 503.
Richards, E. S., and A. W. Palmer, antimony tannate, 933.
Riche, A., action of light on silver chloride, 694.
Richet, C., conditions of lactic fermentation, 663.
Richter, V. v., action of phosphorus pentachloride on ethyl oxalate, 138.
Rickmann, R., constitution of ultramarine, 203, 1014.
Rickmann, J. P., manufacture of ammonia, 496.
Riecke, E., the electromotive power of a Grove's element in terms of Siemens-Weber units, 998.
Riessmüller, L., and N. Wiesinger, conversion of rags and hair into manure, 859.
Rigaut. See Lescœur.
Rilliet. See Ador.
Rinne, A., ultramarine, 885.
Riobinine and A. Saytzeff, diallyl-isopropylcarbinol, 612.
Ritter, A., the "temperature surface" of carbonic acid, 195.
Ritter. See also Cloüet.
Ritthausen, H., albuminoïds from castor-oil seeds, 390.
Roberts. See Gerland.
Rodewald, H., and R. Tollens, reduction of cupric oxide by milk-sugar, 217.
Rodwell, G. F., and H. M. Elder, effect of heat on mercury di-iodide, 498.
Roemer. See Schunck.
Rössler, C., estimation of manganese, 746.
Rössler. See also Gerichten.
Rollet, A., determination of sulphur in the ore, in the fuel, and in the products of the iron industry, 974.
Rosenfeld, M., cuprous chloride, 693.

Rosenfeld. See also Hönig.
Rosenstiehl, A., absorption spectrum of alizarin and of some colouring matters derived from it, 807.
—— anthraflavone and anthraxanthic acid, 383.
—— constitution of the rosanilines, 463.
Rosicki. See Meyer.
Rouville, P. de, natural crystals of magnesium sulphate (epsomite) of large size, 358.
Rudneff, W., action of iodine on thiocarbamides, 48.
—— amides of tertiary hydrocarbon radicles, 713.
—— trimethylcarbamine, 40, 141.
Rudolph, C., benzylamine, 921.
—— derivatives of orthonitraniline, 921.
Rüdorff, F., determination of the specific gravity of powdered substances, 669.
Rügheimer. See Ladenburg.
Ruffle, J., estimation of nitrogen, 961.
Rump. See Jannasch.
Ruoff. See Zetter.
Rush, W. B., copaibic acid, 1038.
Russell, J. C., occurrence of a solid hydrocarbon in the eruptive rocks of New Jersey, U.S.A., 896.

S.

Saarbach, L., phenyloxypropionic acid, 642.
Sabatier, P., thermochemical study of the alkaline sulphides, 865.
—— thermochemical study of dissolved alkaline sulphides, 866.
Sabine, R., motions produced by dilute acids on some amalgam surfaces, 431.
Sachtleben. See Schmidt.
St. Claire-Deville, H., density of the vapour of ammonium dihydrosulphide, 880.
St. Meunier, artificial crystallisation of orthose, 359.
Salkowski, E., behaviour of ammonium chloride in the organism, and estimation of chlorine in urine, 830.
—— compounds of grape-sugar with cupric hydrate, 778.
—— pancreatic digestion, 814.
Salkowski, E. and H., formation of hydrocinnamic acid by means of pancreas ferment, 465.
—— physiological relations of phenylacetic and phenylpropionic acid, 662.
Salkowski, H., behaviour of metanitranisoïl towards ammonia, 528.
—— products of the fermentation of albuminoïds, 659.
Salomon, G., occurrence and origin of hypoxanthine and lactic acid in the animal body, 176.
Salomon. See also Krause.
Salzer, T., hypophosphoric acid and its salts, 105.
Sandberger, F., occurrence of tin in silicates, 608.
Santos, J. R., analysis of lamp-black made from the natural hydrocarbon gas of the Ohio petroleum region, 97.
Sarauw, action of acetic anhydride and sodium acetate on quinone, 718.
Sarrau and Vieille, decomposition of gun cotton in a closed vessel, 991.
Sauer. See Staedel.
Saytzeff, A., action of dilute sulphuric acid on allyldimethyl carbinol, 447.
Saytzeff, A. and P., preparation of dipropylallyl carbinol, 136.
Saytzeff, A. and P., and A. Nikolsky, action of sulphuric acid on allyldimethylethyl- and allyldipropyl-carbinol, 214.
Saytzeff, A., and Schirokoff, diethylallylcarbinol, 214.
Saytzeff. See also Riobinine, Semlianitzine, and Schirokoff.
Schaer, E., decomposition of the haloïd salts of mercury, 694.
Schaffer. See Nencki.
Schaffert, F., experiments on manuring, 1050.
Schalfeeff, melissic acid, 782.
Schall, C., the hydroxytoluic acids from the three isomeric cresols, 791.
Schaumann, N., paraxylidine, 51.
Schaumann. See also Hübner.
Schering, E., lead in potassium iodide, 504.
—— manufacture of potassium iodide, 504.
Schertel, A., grey modification of tin, 888.
Schiel, J., fermentation, 663.
—— formation of ozone by hydrocarbons, 592.
Schiff, H., analysis of organic compounds containing halogens or nitrogen, 555.
—— digallic acid, 466, 646.
—— preservation of potable water, 85, 1072.
—— tungsten oxychlorides and chlorides, 888.
Schiff, R., action of aldehydes on chloral ammonia, 452.

Schiff, R., metanitrocinnamic acid, 321.
—— synthesis of metanitrocumaric acid, 157.
Schiff, R., and G. Tassinari, two monobromopyromucic acids, 308.
Schirokoff, and A. Saytzeff, allyldiethylcarbinol, 448.
Schirokoff. See also Saytzeff.
Schmidt, A., decomposition of hornstone, 511.
—— quartz diorite from Yosemite, 512.
Schmidt, E., mercurialine (methylamine), 40.
—— methylcrotonic and angelic acids, 617.
Schmidt, E., and R. Sachtleben, isobutylformic acid (inactive valeric acid), 139.
Schmidt, H., and G. Schultz, azo-, azoxy- and hydrazo-compounds, 630.
—— —— diphenols, 651.
—— —— diphenyl bases, 252, 652.
—— —— diphenylbenzenes, 163.
Schmidt. See also Barth, and Weidel.
Schmidt, G. A., nitrophenanthrene and its derivatives, 941.
Schmiedeberg, O., a new carbohydrate, 779.
Schmiedeberg, O., and Walter, formation of urea in the animal organism, 952.
Schmitt, E., testing bees'-wax for rosin, 283.
—— the volatile acid of croton oil, 221.
Schmitt, R., constitution of dichlorazophenol, 924.
—— preparation of azobenzene from aniline, 313.
Schmitt, R., and Goldberg, action of bleaching powder on ethyl alcohol, 910.
Schmitt, R., and O. Mittenzwey, action of diazo-compounds on ethyl mercaptan, 304.
Schmitt, R., and R. Möhlau, azoxy-, azo- and hydrazo-phenetols, 317.
Schmitz, H. J., substitution-products of mesitylenic acid, 155.
Schmitz, A., diphenylene ketone and phenylbenzoic acid, 164.
Schmitz. See also Fittig.
Schmoeger, M., isomalic acid, 618.
—— on the possibility of replacing the carbonic acid of the air necessary for the production of chlorophyll in sarcophytic and parasitic plants by organic substances, 737.
Schneider, R., atomic weight of antimony, 354.
Schönberg. See Sonntag.
Schöne, E., electrolysis of hydrogen peroxide, 878.
—— estimation of hydrogen peroxide, 740.
—— hydrogen peroxide, 353, 592.
Schopp. See Hell.
Schorlemmer. See Dale.
Schott, O., estimation of iodine in varec, 1051.
Schraube. See Caro.
Schrauf, A., the tellurium ores of Siebenbürgen, 897.
Schreder, J., fluoresceïn-carboxylic acid, 53.
Schreder. See also Barth.
Schreiner, L., boiling points of the ethereal salts of hydroxy- and alkyloxy- acids, 522.
Schreiner, P., a new organic base in the animal organism, 72.
Schroeckinger, v., dietrichite, a new alum from Hungary, 440.
Schroeder, H., law of molecular volumes, 197, 198, 430.
—— specific gravity determinations of solid organic compounds, 610.
—— volume constitution of the sulphates, selenates, and chromates of the magnesium metals, 768.
Schröder, W., estimation of nitrogen in urine, 829.
Schrodt, M., composition of mare's milk, 550.
Schüler, J., ferricyanides, 702.
Schützenberger, P., researches on albumin, 542.
Schützenberger, P., and A. Destrem, composition of beer-yeast, 477.
—— —— on alcoholic fermentation, 550.
—— —— researches on beer-yeast, 476.
Schulerud, L., on chromates and dichromates, 298.
Schultz, E., specific rotatory power of isocholesterin, 634.
Schultz, G., constitution of phenanthrene, 538, 653.
Schultz. See also Anschütz and Schmidt.
Schultze, W., the malt test, 569.
Schulz, H., action of cacodylic acid on the animal organism, 476.
—— action of mono- and di-phenylarsenic acid on animals, 476.
Schulze, E., and J. Barbieri, lupinin, a new glucoside, 467.
Schumacher, E., granular plagioclase in the limestone strata of Geppersdorf, 902.
—— growth phenomena on quartz crystals from Krummendorf, near Strehlen, 901.

Schumacher, E., idocrase in the limestone strata of Deutsch Tschammendorf, 902.
Schunck, E., indigo-blue, 532.
Schunck, E., and H. Roemer, metabenzdioxyanthraquinone, 68.
—— —— α- and β-nitroalizarin and β-amidoalizarin, 654.
—— —— nitroalizarin, 725.
Schwal. See Medicus.
Schwarz, composition of pyropissite, 1021.
Schwarz, H., formula of hipparaffin, 650.
Seegen, J., transformation of glycogen by the salivary and pancreatic ferments, 548.
Seelig, E., derivatives of mucic acid, 783.
Seidler. See Liebermann.
Selmi, F., formation of poisonous alkaloïds in the human corpse, 734.
—— poisonous alkaloïd from an exhumed corpse, 734.
Semlianitzine and A. Saytzeff, oxyvaleric acid from allyl dimethyl carbinol, 618.
Sendtner, R., action of ethyl oxalate on dimethylparaphenylenediamine, 627.
—— some new salts of uranyl, 507.
Sestini, F., the glucoside of liquorice, 727.
Settegast, H., contributions to quantitative spectrum analysis, 828.
Seubert, C., atomic weight of iridium, 125.
—— double salts of diad iridium, 125.
Shadwell. See Claisen.
Sicherer. See Franchimont.
Sieber. See Nencki.
Siebold, L., titration of hydrocyanic acid and cyanides, and its relation to alkalimetry, 486.
Siegfried. See Albert.
Siewert, E., analysis of hops, 957.
—— estimation of fatty matters in feeding stuffs, 558.
Simon. See Hübner.
Simonin, L., a new process for the treatment of iron and copper pyrites in the dry way, 563.
—— the part played by coal-dust in producing explosions in coal mines, 98.
Skraup, Z. H., cinchonine and cinchonidine, 71.
—— composition of cinchonine, 948.
—— constitution of cinchonine bases, 810.
—— oxidation-products of cinchona bases, 656.
—— oxidation-products of cinchonine, 948.
Skraup, Z. H., oxidation-products of quinine, 809.
Skraup, Z. H., and G. Vortmann, cinchonicine, 948.
Smetham, A., composition of boiler incrustation, 839.
Smith, A. J., halogen-derivatives of β-naphthol, 722.
—— blue flame from common salt, 497.
Smith, E. F., electrolytic estimation of cadmium, 746.
Smith, E. J., electrolytic estimation of cadmium, 276.
Smith, J. J. See Mills.
Smith, J. L., a new earth of the cerium group, and on the analysis of natural niobates, 12.
—— crystals extracted from cast-iron by ether, 771.
—— daubreelite, the new meteoric mineral, 33.
—— remarkable specimen of silicon iron, 204.
—— the native iron of Greenland and the dolerite which encloses it, 892.
—— the supposed new element mosandrium, 13.
Smith, J. L., and L. de Boisbaudran, spectrum of didymium nitrate, 861.
Smith, R. A., absorption of gases by charcoal, Part II, on a new series of equivalents or molecules, 500.
—— detection of fire damp, 991.
Smith, W., characteristic reactions of the aromatic hydrocarbons with antimony or bismuth trichloride, 831.
—— extinguishing fires in tar distilleries, 1080.
—— vapour-densities of the three isomeric dinaphthyls, 537.
Snyders, A. J. C., chemical action of water and saline solutions on zinc, 11.
Sokoloff, N., explosion of nitromannitol, 1080.
—— preparation of nitromannite and the conditions of its explosion, 777.
Solvay, E., preparation of chlorine and hydrochloric acid by means of calcium and magnesium chlorides, 8.
Sommaruga, E. v., action of ammonia on isatin, Part II, 63.
—— action of ammonia on quinones, 718.
—— molecular weight of indigo, 532.
—— vapour-density of indigo, 63.
Sonntag, E., M. Schönberg, and H. Lorenz, feeding experiments with sheep, 951.
Soret, J. L., fluorescence of the salts of the earth-metals, 862.
Soxhlet, F., quantitative estimation of milk fat, 1068.

Soyka, J., influence of soils on the decomposition of organic substances, 339.
Spica, P., propylphenols and other derivatives of propylbenzene, 631.
Spiegelberg, L., nitro-, amido-, and bromo-benzenesulphonic acids, 796.
Spiegelberg. See also Henzelmann.
Spitzer, F. V., camphene from camphor, and its homologues, 168.
—— camphor dichloride, 168.
Stackmann. See Doebner.
Staedel, W., benzophenone, 318.
—— halogen-derivatives of ethane, 368.
—— halogen-derivatives of ethane and ethylene, 212.
—— racemic acid, 223.
Staedel, W., and G. Damm, bromonitro- and bromamido-anisol, 239.
Stäedel, W., and E. Halm, apparatus for regulating the atmospheric pressure in boiling-point determinations, 346.
Stäedel, W., and Kleinschmidt, isoindol, 252.
Staedel, W., and E. Sauer, dinitrobenzophenone, 242.
Stahlschmidt, C., polyporic acid, 382.
Stahre. See Dragendorff.
Stead, J. E., phosphorus in Cleveland ironstone and in iron, 90.
Stefan, diffusion of carbonic anhydride through water and alcohol, 347.
Steffens, Manoury, Mateyczek, and Drevermann, recovery of sugar from molasses, 844.
Stein, G., analysis of Turkey-red oil, 984.
Steinau, R. and C., manufacture of a red pigment from iron scrap, 97.
Steiner, J., the ammoniacal copper test and its application, 1066.
Stevenson, W., estimation of quinine in *ferri et quinæ citras*, B.P., 405.
Stillman, J. M., bernadinite, a resinous mineral from California, 603.
Stingl, J., valuation of burnt lime, 400.
Stingl, J., and T. Morawski, production of sulphur from sulphurous acid and hydrogen sulphide, 1012.
Stingl. See also Morawski.
Stock, W. F. K., analysis of boiler feedwaters, 273.
Stoddart, W., the logwood test for alum, 483.
Stöckenius, O., phenylamidacetic acid, 322.
Stoeder, W., estimation of the alkaloïds in the Bolivian quinine barks exhibited at the Horticultural Exhibition in Amsterdam, 281.
Stohmann, F., a calorimetric method, 586.
Storer, F., and D. S. Lewis, analysis of shave grass, 956.
—— —— analyses of some species of the gourd family, 961.
—— —— analyses of weeds used as salad, 821.
—— —— seed of *Sorghum vulgare*, 956.
Strecker. See Lippmann.
Streng, A., sulphide of silver from Andreasberg, 440, 898.
Stünkel, C., daphnetin, 469.
Stutzer, A., preparation of pressed yeast as a bye-product from potato-spirit, 843.
Suida, W., isatin derivatives, 937.

T.

Tacchini, M., ferruginous particles deposited by a sirocco at certain places in Italy, 515.
Takácz, A., oxidation in the organism, 814.
Tanret, C., alkaloïds of the pomegranate, 657.
—— pelletierine, a base from the bark of the pomegranate, 170.
Tappeiner, H., action of potassium dichromate and sulphuric acid on cholic acid, 388.
Tassinari, G., derivatives of arachidic acid, 307.
Tassinari. See also Schiff.
Tattersall, J., new test for papaverine, 1067.
Tedeschi, V., resorcinoldisulphonic acid, 934.
Terreil, A., analyses of metallic fragments obtained from Peruvian tombs at Arreon (Lima), 409.
—— new determination of the equivalent of aluminium, 692.
—— new method for determining the melting point of organic substances, 673.
Textor. See Gabba.
Treiber. See Lintner.
Thaer, experimental inquiry as to the quantity of nitrogen which must be supplied to cultivated plants to ensure their normal development as field crops, 668.
Theodor. See Voit.
Thörner, W., and T. Zincke, diphenylmethylacetic acid, 322.
—— —— pinacones and pinacolines, Part IV, 317.
Thollon, L., displacement of the lines

of the spectrum by the motion due to the sun's rotation, 574.
Thomas, J. W., composition of the gas which issued from one of the shafts of Abercarn Colliery, 357.
Thomsen, A. L., action of potassium cyanate on epichlorhydrin, 217.
Thomsen, J., accuracy of thermochemical results, 433.
—— composition of precipitated copper sulphide, 206.
—— heat of formation of metallic sulphides, 433.
—— monohydrated sodium sulphate and dihydrated sodium carbonate, 194.
—— thermochemical researches: heat of solution of nitrates, sulphates, dithionates, and some other salts, 6.
—— zinc sulphydrate, 206.
Thomsen, T., composition of wood, 613.
Thomson, J. S., preparation of distilled water free from ammonia, 878.
Thomson, W., the ferment produced by the morbid growth of the bioplasm of the yolk of egg, 478.
Thoms, G., teak wood, 996.
Thresh, J. C., detection and approximate determination of minute quantities of alcohol, 279.
Tichborne, C. R. C., some peculiarities of the Vartry waters, and the action of that water on boiler-plates, 85.
Tiemann, F., relation between the xylenols and some other hydroxy-derivatives of benzenes, 924.
Tiemann, F., and E. Helkenberg, aldehydes from orcinol and their derivatives, 719.
Tiemann, F., and L. Landshoff, aldehyde-hydroxybenzoic acid, 927.
Tiemann, F., and C. L. Reimer, umbelliferone derivatives, 720.
Tiemann. See also Baumann.
Tilden, W. A., an examination of distilled essence of lemon, 386.
—— compounds of the terpenes with hydrochloric acid, 943.
—— determination of specific gravities, 197.
Tönnies, P., action of nitrosyl chloride on unsaturated hydrocarbons, 517.
—— action of nitrous acid on unsaturated hydrocarbons, 35.
—— conversion of furfurangelic acid into azelaic acid, 915.
—— relation of dibromopyromucic acid to mucobromic acid, 918.
Tollens, B., oxidation of levulinic acid, 523.
Tollens, B., specific rotatory power of cane-sugar, 136, 557.
Tollens. See also Dieck and Rodewald.
Tornöe, H., results of the Norwegian expedition to the North Sea, 1060.
Trippke, P., the enstatite in the olivine nodules of the Gröditzberg, 514.
—— the twin formation of phillipsite, from Sirgwitz, 515.
Trompetter. See Bernthsen.
Troost, L., basic hydrosulphides of ammonia, 880.
—— distillation of a heterogeneous liquid, 875.
—— employment of diffusion in the study of the phenomena of dissociation, 1006.
—— maximum tension and vapour-density of alizarin, 1039.
—— new compounds of hydrochloric acid with ammonia, 501.
—— vapour-densities of high boiling organic compounds, 1025.
Trümpler, E., action of soda solution on picramic acid, 717.
Tschaplowitz, F., absorption of water by leaves, 819.
Tschermak, G., pelagosite, 604.
Tschermak. See also Buchner and Grimaux.
Tweedie, G. R., new method of producing a coating of magnetic iron oxide on iron surfaces, 840.

U.

Ullik, F., absorptive power of soils, 667.
—— gelatinous silica as an inorganic membrane, 199.
—— agricultural experiments on irrigated land, 825.
Urbain and Renoul, a compound of alumina with carbonic acid, 885.
Urech, F., action of potassium carbonate on isobutyl aldehyde, 520.

V.

Valente. See Cannizzaro.
Valitsky, action of aniline, toluidine, and naphthylamine on chloresteryl chloride, 376.
Varenne, L., compound of chromic acid with potassium fluoride, 1016.
—— formation of crystalline metallic

oxides by means of potassium cyanide, 1016.
Vaucher, G., ly-chô, a new thickening material, 187.
Vedova, F. G., improvements in the manufacture of materials containing tannic acid, 496.
Vibrans, G., choice of beet-root for seed, 822.
Vieille. See Sarrau.
Vielhaber, H. C., application of phenol phthaleïn, 273.
—— estimation of hydrocyanic acid in bitter-almond water, 280.
Villiers, A., analysis of honey from Ethiopia, 450.
Villari, E., thermic and galvanometric laws of the electric spark, 576.
Vincent, C., distillation of beet-root residues, 913.
—— presence of nitrites in the distillate obtained by the calcination of residues from beet-root molasses, 612.
Vincent, C., and Delachanal, density and coefficient of expansion of liquid methyl chloride, 294.
Violle, J., radiation from incandescent platinum, 573.
—— specific heat and latent heat of fusion of palladium, 294.
Vogel, H. W., difference in the absorption spectra of one and the same substance, 189.
—— photographed spectra of oxygen and hydrogen, 497.
—— testing alizarin colouring-matters and green aniline colours, 83.
Voglor, H., composition of commercial ammonium carbonate and of the product formed on exposing it to air, 354.
Vohl, H., mineral spring "Marienbrunnen," near Iserlohn, Westphalia, 211.
—— Ofner Radóczy-bitterwater, 211.
Voit, C., influence of the temperature of the surrounding air on the processes of decomposition in the organism of warm-blooded animals, 75.
Voit, C., and C. Theodor, influence of the surrounding temperature on the tissue metamorphosis of warm-blooded animals, 951.
Vortmann, G., cobalt-ammonium compounds, 438.
Vortmann. See also Lippmann.
Vulpius, G., formation of mercuric from mercurous chloride, 889.
—— mechanical purification of mercury, 125.
—— salicylates and their application, 641.
Vulpius, G., solubility of sulphur and phosphorus, 104.

W.

Waage, P., the ebullioscope, 1065.
Waage. See also Guldberg.
Wagner, R. v., numeïte, a new jewel, 184.
Walitzky, W., derivatives of brain cholesterin, 135.
Wallace, R. W., and C. F. Claus, application of gas-liquor to the production of potassium carbonate and other salts, 677.
Wallach, O., chloralide and its derivatives, 43.
—— organic thio-compounds, 312.
Wallach, O., and O. Bischof, decomposition of dichloracrylic acid by alkalis, 453.
Wallach, O., and H. Bleibtreu, thio-derivatives, 786.
Wallach, O., and P. Pirath, thiamides of the oxalic acid series, 784.
Waltenhofen, A. v., magnetic behaviour of finely-divided iron, 1000.
Walter. See Schmiedeberg.
Wanklyn, J. A., and W. J. Cooper, the moist-combustion process, 555.
Warden, C. J. H., composition of poppy-petal ash, 395.
Wartha, V., hectograph and chromograph, 836.
—— preliminary note on the analysis of the Zsadányer meteorite, 210.
Wasowicz, M. v., Verryken's method of detecting metallic poisons, 973.
Wassermann, M., derivatives of methyleugenol, 790.
Watson, W. H., detection of milk adulteration, 1068.
Wattenberg, H., estimation of soluble phosphoric acid in superphosphates, 672.
Weber, R., behaviour of tin and lead alloys with vinegar, 990.
—— composition and durability of glass, 754.
Weber, W., detection of indican in urine, 343.
Weidel, H., berberine, 656.
Weidel, H., and M. v. Schmidt, formation of cinchomeronic acid from quinine, and its identity with pyridene-carbonic acid, 947.
Weigelt, C., Dochnahl's new method of preparing wine, 569.
—— the time of first racking-off new wines, 569.

Weigert, L., clarifying and preserving wine, 290.
—— estimation of acetic acid in urine, 980.
Weil, F., further note on Weil's volumetric method of estimating copper, 276.
Wein, E., estimation of soluble phosphoric acid in superphosphates, 745.
—— feeding calves without the cow's milk, 1046.
Wein, E., and E. Ebermann, manure experiments with bone meal, superphosphate, and with potash salts, 959.
Weinberg. See Jacobsen.
Weisbach, A., cacochlor from Rengersdorf, near Görlitz, 901.
Weisinger. See Riessmüller.
Weith, W., synthesis of carbotriphenyltriamine, 462.
Weith. See also Merz.
Weitz, M., crystallisation of sugar and preparation of sugar-candy, 844.
Werigo and Melikoff, monochlorolactic acid and dichloropropionic acid from glyceric acid, 521.
Weselsky, P., and R. Benedikt, azophenols, 718.
Weyl, T., creatinine and creatine, 471.
—— decomposition of tyrosine by putrefaction, 541.
Whewell, G., analysis of bleaching powder, 505.
—— tenacity of starch, 570.
Wichmann, A., the sericite rocks of the Taunus, 23.
Widmann, O., action of chlorine on naphthalene β-sulphonic chloride: a new trichloronaphthalene, 722.
—— dichloronaphthalene β-sulphonic acid, 722.
Widnmann, E., isomeric nitro- and amido-benzoic acids, and formation of chloranil from the latter, 154.
Wiebe, H. F., expansion of solid and fluid bodies, 1002.
—— thermo-chemical relation between the boiling and melting points of solid elements, 690.
Wiedemann, G., dissociation of dissolved ferric salts, 348.
Wiesinger. See Muller.
Wigman. See Franchimont.
Wigner, G. W., nitrogen compounds present in cereals, 486.
—— nitrogenous constituents of cocoa, 493.
—— on Cleopatra's needle, 445.
—— some experiments with silicated carbon and spongy iron filters, 493.
Wilckens, M., digestion in the different divisions of the digestive canal of the sheep, 391.
Wildt, seeds of *Lallemantia iberica*, 822.
Wilkes, J., and T. Johnson, improvements in purifying or refining copper, 423.
Willgerodt, C., action of the basic compounds on solutions of α-dinitrochlorobenzene in carbon bisulphide, 714.
—— ethers of trinitrophenol, 923.
—— preparation of ethers of α-dinitrophenol from α-dinitrochlorobenzene, 716.
Williams, G., substitute for litmus, 553.
Willm, E., mineral waters of Auvergne, 446.
—— presence of mercury in the mineral waters of Saint Nectaire, 697.
Wilson, H. M., remarks on the estimation of calcium sulphate in beer, 79.
Winkelmann, A., deviation of some gases from Boyle's law, 346.
Winkler, C., fire damp in collieries, 760.
Witt, O., presence of ethyl alcohol in coal tar, 136.
Wittmak, L., action of the sap of *Carica papaya*, 1048.
—— advantages of only partially removing the fat from oil seeds, 99.
Witz, A., thermic effect of the walls of closed vessels on the contained gases, 432.
Witz, G., inactivity of chromium compounds in producing aniline black as compared with the action of vanadium compounds, 421.
—— value of certain chemical agents in dyeing with aniline-black, 684.
Wolff. See Doebner.
Wolffhügel, G., carbon monoxide in foundry furnaces, 344.
Wolfram, G., nitro-compounds of cellulose, 218.
—— nitro-derivatives of cellulose, 371.
—— quantitative determination of theobromine in cacao and chocolate, 406.
Wollny, E., ridge cultivation, 822.
—— temperature of soils, 824.
Wreden, F., camphor, 69.
Wroblewsky, E., mineral waters of the Couban in the Caucasus, 125.
—— separation of orthoxylene from its isomerides, and a new xylidene, 919.
—— structural formula of aromatic compounds, 526.
Wullner, A., relation between the specific heat at a constant volume, the temperature and the conductivity of gases, 2.

Wurster, C., methyl-derivatives of paraphenylenediamine, 626.
—— nitrodimethylaniline, 626.
—— quantitative estimation of starch in paper, 180.
Wurster. See also Fittig.
Wurtz, A., bases derived from aldol-ammonia, 704, 780.
—— chloral hydrate, 914.
Wurtz, A., and E. Bouchut, digestive ferment of *Carica papaya*, 1048.

Y.

Young, W. C., note on the detection of alum in flour by the logwood test, 483.

Z.

Zeidler, O. and F., action of oxidising agents on the olefines, 907.
Zeisel. See Lieben.
Zepharovich, V. v., magnetite from Monte Mulatto, S. Tyrol, 23.
—— new mineral occurrences in the iron ore district of Moravicza, in the Banat, 363.
—— mirabilite from Aussee, 23.
—— yellow dolomite from Bleiberg, 19.
Zerener, H., method of preventing house-fungus, 1080.
Zetter, H. H., Ruoff and Möe, researches on perchlorination, 721.
Zetter. See also Merz.
Zimmermann. See Gabriel; also Muchler.
Zincke. See Breuer; also Thörner.
Zorn, W., action of nitrosyl silver, 309.
—— diazo-compounds of the fatty series, 221.
Züblin, H., synthesis of isosuccinic acid, 783.
Zulkowsky, C., aurin, 58.
—— diastase and beet mucilage, 660.

INDEX OF SUBJECTS.

ABSTRACTS. 1879.

A.

Absorption of selenium by plants, 955.
Absorption-spectra, differences in, 189.
—— —— of didymiferous minerals, measurement of, 697.
Absorption-spectrum of alizarin and of some colouring matters derived from it, 807.
—— —— of nitro-alizarin, 807.
—— —— of pseudo-purpurin, 807.
—— —— of purpurin, 807.
Acetal, monochlor-, action of bleaching powder on, 910.
Acetamide, monobrom-, 221.
Acetic acid, absorption of hydrobromic acid by, 705.
—— —— absorption of hydrochloric acid by, 705.
—— —— action of bromine on, 705.
—— —— addition-products of, with bromine and hydrochloric acid, 705.
—— —— derivatives, heat of formation of, 872.
—— —— estimation of, in wine, 980.
—— —— formation of, by yeast alone, in presence and absence of oxygen, 663.
—— —— occurrence of furfuraldehyde, in glacial, 137.
Acetic anhydride, action of aluminium chloride on, 620, 915.
—— —— action of ammonia on, 621.
—— —— chemical functions of, 621.
—— —— action of reducing agents on, 621.
—— —— action of sodium-hydrogen sulphite on, 621.
Acetobromhydrin, action of zinc-copper couple on, 1030.
—— preparation of, 1030.
Acetonaphthylthiamide, 147.
Acetone, action of boron fluoride on, 914.
—— action of methylamine on, 1035.
—— bor-, 915.
—— fluobor-, α- and β-, 914.
—— preparation of hexmethylbenzene from, 940.
Acetophenone, reduction of, 61.
—— a sulphuretted derivative of, 61.
—— thio-, 61.
Acetopropionic acid and lævulinic acid, identity of, 453.
Acetoquercites, 240.
Acetothiotoluidide, 147.
Acetotoluide [1 : 4], dimorphism of, 626.
Acetoxylide, 920.
Acetumbelliferone, 721.
Acetylbutylchloral cyanide, 41.
Acetyldimethylparaphenylene-diamine, 627.
Acetylene, action of sulphuric acid on, 780.
—— liquid, physical properties of, 1028.
—— carbamides, 142.
—— chlor-, 453.
—— isopropyl-, 134.
Acetylformamide, 45.
Acetyl mucobromate, 224.
—— pyromeconate, 709.
Acid, free, estimation of, in tan-liquors, 980.
—— organic, a new, from bromocitraconic acid, 1037.
Acidimetry, a new indicator for use in, 396.
Acids, action of, on salts, 689.
—— aqueous, with constant boiling points, vapour-density of, 579.
—— aromatic, fusion of, with soda, 926.
—— detection and estimation of nitrous acid in, 964.
—— nitrogen, behaviour of, with sulphuric acid, 770.
—— obtained by distilling the crude acids derived from the saponification of neutral fatty bodies in a current of superheated steam, 1036.
—— of wood-vinegar, 43.
—— produced by the introduction of chloro- and bromo-benzene into the animal system, 796.
Aconitine, colour reaction with antimony trichloride, 832.
Acrylic acid, chlorobrom-, 616.

Acrylic acid, dibrom-, 373, 616.
—— —— dibrom-, and its salts, 224.
—— —— dichlor-, 616.
—— —— dichlor-, decomposition of, by alkalis, 453.
—— —— di-substitution derivative of, 616.
—— —— dimethyl-, an isomeride of angelic acid, 782.
—— —— iodobrom-, 616.
Addition-products of nitro-compounds, 50.
Adipic acid, hydroxy-, preparation of, 706.
Adular from Verespatak, 359.
Agricultural products, estimation of nitrogen in the analysis of, 962.
Air, bye-products obtained in the ozonisation of, by moist phosphorus, 881.
—— contained in sea-water, 1060.
—— estimation of carbonic acid in the, 78.
—— explosive mixtures of, with combustible powders, 412.
—— presence of an alcoholic ferment in, 394.
—— proportion of carbonic anhydride in, 744.
Air-baths, gas regulator for, 294.
Albumin, action of baryta on, 542.
—— alkaloïds from putrefied, 734.
—— aromatic products of the putrefaction of, 806.
—— complete precipitation of, from animal fluids, 183.
—— compounds, crystalline, preparation of, 950.
—— determination of ammonia in, 542.
—— fermentation of, 664.
—— of the refracting media of the eye, 834.
—— oxidation of, by the oxygen of the air, 389.
—— reactions of, 834.
—— regeneration of, from peptone, 950.
—— researches on, 542.
—— volatile oil obtained by the action of baryta on, 543.
Albuminoïd compounds of the organs, and of the spleen in particular, 175.
—— matter, putrefying, formation of phenol from, 1037.
—— substances injected into the veins, modification of, by the animal organism, 334.
Albuminoïds, decomposition-products of, 389.
—— from castor-oil seeds, 390.
—— gas evolved by the action of barium hydrate on, 735.
Albuminoïds of gourd seeds, 272.
—— products of the fermentation of, 659.
Albumins, nature of, in hydrocele, 550.
Alcohol, action of, on bacteria, 817.
—— detection and approximate determination of minute quantities of, 279.
—— ethyl, action of, on ethyl chlorosulphonate, 776, 777.
—— formation of, by yeast alone, in presence and absence of oxygen, 663.
—— in beer, estimation of, by means of the ebullioscope, 1065.
—— limit of separation of, from water, by distillation, 703.
—— products from crude, 612.
—— radicles, action of water on the haloïd compounds of, 700.
—— transformation of sugar into, 778.
Alcohol-hydroxybenzoic acids, xylenols, homo-oxybenzyl alcohols, hydroxytoluic aldehydes and acids, aldehydehydroxybenzoic acids, and hydroxyphthalic acids, relation between, 924.
Alcoholic ferment, soluble, non-existence of, 1046.
—— fermentation, 550.
Alcohols, fatty, diagnosis of, 673.
—— in potato fusel-oil, 36.
—— polyhydric, ethereal sulphates of, 1033.
—— primary, etherification of, 36.
—— secondary, etherification of, 214.
—— tertiary, etherification of, 215.
Aldehyde, conversion of, into mercaptan, 451.
—— formation of, in alcoholic fermentation, 551.
Aldehyde-green, 84.
Aldehyde-hydroxybenzoic acids from metahydroxybenzoic acid, 927.
—— ——, xylenols, homo-oxybenzyl alcohols, hydroxytoluic aldehydes and acids, alcohol-hydroxybenzoic acids, and hydroxyphthalic acids, relation between, 924.
Aldehydes from orcinol, and their derivatives, 719.
Aldehydines, simple mode of preparing, 233.
Aldol, action of ammonia on, 780.
Aldol-ammonia, bases derived from, 704, 780.
Ales, Burton, and Dublin porter, analysis of, 344.
Alizarin, absorption-spectrum of, 807.
—— β-amido-, 654.
—— colouring matters, 83.
—— diamide or diamidanthraquinone, 254.

Alizarin, from α-diamidanthraquinone, 724.
—— maximum tension of, 1039.
—— nitro-, 725.
—— nitro-, absorption-spectrum of, 807.
—— α- and β-nitro-, and its derivatives, 654.
—— nitroso-compounds of, 383.
—— vapour-density of, 1039.
β-Alizarinamide, or amiderythro-oxyanthraquinone, 253, 254.
Alizarin-blue, 83, 259, 419.
—— —— base from, 259.
—— —— synthesis of, 259.
Alizarin-orange (nitro-alizarin), 84.
Alizarin-purpuro-sulphonic acid, 256.
Alizarin-sulphonic acid, 655.
Alizarin-sulphonic acids, 256.
Alkali, improvements in the manufacture of, 422.
Alkali-albuminate, 489.
Alkali-blue, 418.
Alkali-metals, amalgams of, 864.
—— —— amalgams of, heat of formation of, 884.
—— —— amalgams of, heat of oxidation of, 884.
—— —— chemical constitution of amalgams of, 883.
Alkalimetry, a new indicator for use in, 396.
Alkaline aluminates, preparation of, 491.
—— earths, separation of, from the alkalis, 341.
—— resinates and soaps, abnormal solubility of certain bodies in, 99.
—— sulphides, dissolved, heat of formation of, 866.
—— sulphides, thermo-chemical studies of, 865.
Alkalis, separation of magnesium from, 969.
—— separation of the alkaline earths from, 341.
Alkaloïd, new, 658.
—— of Mio-Mio (*Baccharis cordifolia*), 1045.
—— poisonous and crystallisable, from an exhumed corpse containing arsenic, 734.
Alkaloïds, characteristic colour reactions with antimony trichloride, 831.
—— estimation of, in the Bolivian cinchona barks exhibited at the Horticultural Exhibition in Amsterdam, 281.
—— from putrefied albumin, 734.
—— from putrefied eggs, 734.
—— of ergot, contribution to a knowledge of, 387, 269.
Alkaloïds, poisonous, formation of, in the human corpse, 734.
—— quinine, iodosulphates of, 982.
Alkyloxy-acids, boiling points of ethereal salts of, 522.
Allantoic acid, 228, 461.
Allantoïn, constitutional formula of, 227.
—— derivatives of, 228.
Allantoxaidin, 227.
Allantoxanic acid, 226.
Allantoxoïdin, 461.
Allanturic acid, 228, 461.
Alloxan, synthesis of, 375.
Alloxantin, synthesis of, 375.
Alloy of iridio-platinum, 774.
Alloys, analysis of, containing copper, zinc, and nickel, 485.
—— of lead and antimony, 889.
—— used as stopping for teeth, analysis of, 1076.
Allyl borate, action of zinc ethide on, 621.
—— iodide, action of water on, 700.
Allyldiethylcarbinol, 214, 448.
Allyldimethylcarbinol, action of dilute sulphuric acid on, 214, 447.
Allyldipropylcarbinol, action of dilute sulphuric acid on, 214, 447.
Alpine dairy process, 857.
Alstonamine, 71.
Alstonia bark, 332.
Alstonia constricta, further remarks on, 269.
Alum, detection and estimation of, in wheat flour, 483.
—— detection of, in flour by the logwood test, 483.
—— effect of, on bread, 1077.
—— in flour and bread, 556.
—— logwood test for, 483.
Alumina, action of sulphuretted hydrogen on alkaline solutions of, 437.
—— compound of, with carbonic acid, 885.
—— preparation of, 490.
—— and ferric oxide, separation of, from manganese, zinc, cobalt, and nickel, 970.
—— and iron, sesquisulphates of, 594.
Aluminium, new determination of the equivalent of, 692.
—— bromide, compounds of cymene with, 785.
—— chloride, action of acetic and sulphurous anhydrides on, 915.
—— chloride, compounds of cymene with, 785.
—— —— compounds of, with benzene and toluene, 461.
—— —— interpretations of reactions occurring in presence of, 785.
—— phosphates of, 203.

Aluminium sulphate, improvements in the manufacture of, 423.
—— and chromium, sesquisulphates of, 595.
—— and ferric oxides, new method for separating, from manganese, 1055.
—— and manganese, sesquisulphate of, 595.
Alums, etch-figures produced on, 439.
Amalgam of chromium, 693.
—— of cobalt, 693.
—— of iron, 693.
—— of manganese, 693.
—— of nickel, 693.
—— surfaces, motions produced by dilute acids on some, 431.
Amalgams of the alkali-metals, 864.
—— —— chemical constitution of, 883.
—— —— heat of formation of, 884.
—— —— heat of oxidation of, 884.
Amaranthus salicifolius (*caudatus*), colouring-matter of, 730.
Amazonstone (microline), from Pike's Peak, Colorado, 515.
Amber, amount of sulphur in, 300.
—— microscopical properties of, 300.
Amides of tertiary hydrocarbon radicles, 713.
Amidines of monobasic organic acids, 922.
Amidobenzoic acid, carbimid-, formula of, 466.
—— —— cyanocarbimid-, formula of, 466.
—— —— oxethylcarbimid-, formula of, 466.
—— percyanides, 466.
Amido-benzoyl, dicyan-, formula of, 466.
—— oxethylcyan-, formula of, 466.
Amido-deoxybenzoïn, 150.
Amido-isobutylformic acid (isopropylglygocine), 140.
Amido-œnanthylic acid, 1037.
Amines, action of sulphochlorides on, 920.
Ammi visnaga, active principle of, 1040.
Ammonia, manufacture of, 496.
—— new compounds of hydrochloric acid with, 501.
—— purification of gas by, 986.
—— soda process in conjunction with the manufacture of gas, 837.
Ammoniacal copper test and its application, 1066.
—— mercury compounds, 438.
Ammonium amidoglyoxylate, 619.
—— carbonate, composition of commercial, and of the product formed on exposing it to the air, 354.
Ammonium chloride, behaviour of, in the organism, 830.
—— chloride, dissociation of, a lecture experiment, 196.
—— chloride solution, standard, alteration of, when kept in the dark, 400.
—— dihydrosulphide, 880.
—— dimethylamido-azobenzenesulphonate, substitution of, for litmus, 553.
—— formate, decomposition of, by heat, 705.
—— hydrosulphide, dissociation of, 879, 880.
—— hydrosulphides, basic, 880.
—— nitrate, 200.
—— nitrate, production of a high temperature by means of, 102.
—— nitrite, 881.
—— nitrite, formation of, 298.
—— sulphate, fertilising action of, 739.
—— sulphide, dissociation of, 879.
—— thiocyanate, action of chloral hydrate on, 306.
—— lead ferricyanide, 703.
Amydecylenic acid, 521.
Amyl alcohol, dextrogyrate, 369.
—— benzoate, vapour-density of, 1025.
—— cyanate, 913.
—— iodide, 37.
—— nitrite, action of, on blood, 816.
—— pyrrol, 525.
—— thiocarbimide, tertiary, 713.
Amylamine, 517.
Amylene, 37.
—— action of nitrosyl chloride on, 517.
—— action of oxidising agents on, 908.
—— heat of vaporisation of, 874.
—— bromide, action of water on, 700.
Amylidene-aniline, 462, 714.
Amyloïd substance peculiar to the "Asques of Pyrenomycetes," 613.
Amyloïds of the egg, 662.
Amylomycin, 613.
Amyrin, 73.
Anaërobic organisms, conditions of life of, 954.
Analysis, quantitative, use of blowpipe to, 740.
—— use of sulphuretted hydrogen in the dry way in, 963.
Anethoïl, action of nitrosyl chloride on, 517.
Anethol, oxidation of, 320.
Angelactic acid, monochlor-, 42.
Angelactamide monochlor-, 42.
Angelic acid, 617.
—— —— action of hydrobromic acid, on, 455.
—— —— constitution of, 456.
—— —— conversion of, into tiglic acid, 454.

Angelic acid, dimethylacrylic acid, an isomeride of, 782.
—— —— from Roman chamomile oil, 454.
—— —— hydriodo-, 618.
—— —— isomeride of, 706.
—— —— mono- and dichlor-, 43.
Angelic acids of different origin, 45.
Angelic and tiglic acids, separation of, 455.
Angelylamine, 712.
Angelylthiocarbamide, 712.
Angelylthiocarbimide, 712.
Anhydrides, action of dehydrating substances on, 245.
Anhydrorthosulphamine-benzoic acid, 628.
Aniline, action of ethylisothiacetanilide on, 786.
—— action of, on glyoxylic acid, 51.
—— amylidene-, 462, 714.
—— benzoyl-, 716.
—— benzyl-, 147.
—— dichloracetate, 786.
—— chlorate, 785.
—— chloronitr-, 309.
—— dibenzoyl-, 716.
—— dichlor-, symmetrical, 231.
—— dimethyl-, action of chloroform and perchloromethane on, 714.
—— —— action of mercuric chloride on, 231.
—— —— action of trichlormethylsulphochloride on, 920.
—— dinitrodichlor-, 310.
—— dioxydidimethyl-, 714.
—— diothiodidimethyl-, desulphurisation of, 714.
—— hydrochloride, heat of formation of, 767, 871.
—— hydrofluoride, 786.
—— iodate, 786.
—— metadichlor-, 143.
—— methyl-, 494.
—— methyl-, manufacture of, 995.
—— methylated derivatives of, and the colours obtained therefrom, 310.
—— monochloracetate, 786.
—— nitrate, heat of formation of, 871.
—— nitrodichlor-, 309.
—— nitrodimethyl-, 626.
—— nitrotrichlor-, 310.
—— orthonitro-, derivatives of, 921.
—— oxalate, heat of formation of, 871.
—— paradichlor-, 143.
—— paramethylenedidimethyl-, 714.
—— paranitro-, heat evolved by the action of hydrochloric acid on, 872.
—— paranitr-, hydrochloride, heat formation of, 768.
—— perchlorate, 786.
—— phthalate, 786.
Aniline residues, 715.
—— salts, 785.
—— tribrom-, 55, 464.
—— trichloracetate, 786.
Aniline-black, dyeing with, 684.
—— —— formation of, by chromate in presence of chlorates, 495.
—— —— improvements in dyeing and printing, 422.
—— —— inactivity of chromium-compounds in producing, as compared with the action of vanadium compounds, 421.
Aniline-blue, 415.
Aniline-red, utilisation of the residues obtained in the manufacture of, 995.
Anilines, chlor-, 143.
—— chlor-, heat evolved by the action of hydrochloric acid on, 872.
—— compounds of cobalt and nickel chlorides with, 461.
—— monochlor-, three isomeric, heat evolved by the action of sodic oxide on, 768.
—— orthodichlor-, 143.
—— tetrachlor-, 143.
—— trichlor-, 143.
Animal body, synthetic processes in, 176.
—— charcoal filters, experiments with, 986.
—— —— and spongy iron as materials for purifying water, 343.
—— fluids, complete precipitation of albumin from, 183.
—— organism, action of cacodylic acid on, 476.
—— —— action of carbonic anhydride on, 174.
—— —— behaviour of phenol in, 816.
—— —— formation of urea from, 952.
—— —— modification effected by, on various albuminoïd substances when injected into the veins, 334.
—— —— oxidations in, 814.
—— —— syntheses in, 814.
—— system, acids produced by the introduction of chloro- and bromo-benzene into, 796.
—— —— action of bromobenzene on, 803.
—— textile fibres, bleaching process for, 99.
Animals, action of mono- and di-phenylarsenic acids on, 476.
—— existence of bacteria or their germs in the healthy organs of, 1045.
—— herbivorous, source of hippuric acid in the urine of, 952.
—— influence of the temperature of the surrounding air on the processes of decomposition in the organism of warm-blooded, 76.

Animals, warm-blooded, influence of the surrounding temperature on the tissue change of, 951.
Anisidine, bromorth-, and its salts, 239.
Anisidine, dibromorth-, and its salts, 239.
Anisol, bromamido-, 239.
—— bromonitr-, 239.
—— dibromparanitr-, 239.
—— α-dinitr-, 717.
—— metanitr-, 238.
—— monobromortho-nitr-, 239.
Anisols, dinitr-, 238.
—— —— decomposition of, by alcoholic ammonia, 238.
Ankerite from Phœnixville, 604.
Anorthite, pseudomorph after, 1023.
Anthemol, 455.
Anthracene, colour reaction with antimony trichloride, 831.
—— colour reaction with bismuth trichloride, 831.
—— derivatives of the chrysazin series, 537.
Anthracene, perbrom-, 655.
Anthracenedisulphonic acid, 537.
—— —— and its conversion into anthrarufin, 257.
Anthracenehydride-monosulphonic acid, soda salt of, 537.
Anthracite dust, use of, in Du Puy's process, 564.
Anthraflavone, 383.
Anthranilic acid, action of cyanogen on, 321.
Anthrapurpurin, isopurpurin, and flavopurpurin, actual relations of, 943.
Anthraquinone β-acetamiderythroxy-, 254.
—— α-acetamidoxy-, 254.
—— amiderythro-oxy-, or β-alizarinamide, 253, 254.
—— derivatives of, 253.
—— diamid-, or alizarin-diamide, 254, 724.
—— metabenzdioxy-, 68.
—— monhydroxy-, 724.
—— trioxy-, 255.
Anthraquinone-monosulphonic acid, action of potash on, 724.
Anthraquinonesulphonic acid, fusion of, with potash, 943.
Anthraquinone-sulphonic acids, amidoxy-, 255.
—— —— reduction of, 537.
—— —— sodium salts of, 942.
Anthrarufin, 259, 537.
—— constitution of, 942.
—— conversion of anthracene-disulphonic acid into, 257.
—— from anthracene, synthesis of, 260.
—— tetranitro-, 538.
Anthraxanthic acid, 383.
Anthrol, 653, 654.
Antichlor, 676.
Antimony, atomic weight of, 354, 772.
—— recovery of, 491.
—— criticism on Bunsen's older method for separating arsenic from, 1058.
—— chloride, action of sulphuric monochloride on, 201.
—— tannate, 933.
—— trioxide, vapour-density of, 875.
—— and lead, alloys of, 889.
Apatites, analyses of, 695.
Apomorphine, reaction with antimony trichloride, 831.
Apparatus for regulating the atmospheric pressure in boiling point determinations, 346.
Apple wine, 1078.
Aqua phagedænica, solubility of lime in water in reference to the prescription for, 491.
Arachidic acid, some derivatives of, 307.
Aricine, 1043.
Aromatic compounds, hydrogenation of, 376.
—— —— structural formulæ of, 526.
—— —— with long side-chains, action of iodine on, 623.
—— hydrocarbons, bromination of, in presence of aluminium bromide, 142.
Arsenic from antimony, criticism on Bunsen's older method for separating, 1058.
—— in grape-sugar, 1077.
—— test for, 277.
—— acid, separation of, from its salts, 972.
Arsenical pyrites (mispickel), chemical and crystallographical examination of, 900.
Arsenious acid, magnesia as an antidote for, 77.
—— anhydride, vapour-density of, 767.
Artichoke, Jerusalem, carbohydrates of, 778.
Artocarpus speciosus, examination of, 860.
Ashes of wheat-bran, composition of, 961.
Asphalte, Syrian and American, 896.
—— and other retinalites, 301.
Aspidospermine, 470.
Atacamite, 17.
Atomic theory, application of Gaudin's, to certain minerals, 602.
—— —— of heat, 687.
—— weights, determination of, 769.
—— —— use of isomorphism for the determination of, 769.
Atopite, 21.

Atrolactic acid, 379.
Atropic acid, 379.
—— —— bromhydr-, 379.
—— —— hydrotribrom-, 380.
—— —— monobrom-, 380.
Atropine, artificial, 733.
—— reaction with antimony trichloride, 832.
Augite (pyroxene), varieties of, 364.
Auriferous pyrites, examination of, 509.
Aurin, 58, 386, 789, 925.
—— action of ammonia on, 925.
—— action of methylamine on, 926.
—— formation of, from phenol, 789.
—— from dioxybenzophenone, synthesis of, 60.
Australene, formula of, 168.
Azelaic acid, conversion of furfurangelic acid into, 915.
Azobenzene, amido-, 383.
—— amido-, hydrochloride of, 383.
—— preparation of, 630.
—— preparation of, from aniline, 313.
Azobenzenenaphthylamine, 629.
Azo-compounds, remarks on Weselky's and Benedikt's investigation on some, 629.
Azonaphthylene, amido-, 383.
Azophenetols, 317.
Azophenol, dichlor-, constitution of, 924.
—— —— so-called, 315.
Azophenols, 718.
—— tetrabrom-, 718.
Azotoluene, amido-ortho-, 383.
—— preparation of, from toluidine, 313.
Azoxybenzene, action of stannous chloride on, 630.
Azoxy-phenetols, 317.
Azulmin, 1028.

B.

Baccarine, 1045.
Baccharis cordifolia (Mio-Mio), alkaloïd of, 1045.
Bacillus in urine, 817.
Bacteria, action of alcohol on, 817.
—— method of photographing, 1046.
—— occurrence of, in milk, 817.
—— occurrence of, in a potable water, 817.
—— vitality of, 817.
—— or their germs, existence of, in the healthy organs of animals, 1045.
Baking powders, American, 1077.
Balsamum antarthriticum indicum, investigation of, 262.
Banana, 479.
—— utilisation of, 568.
Barbituric acid, (malonyl urea), 460.
Barcenite, a new antimonate, from Huitzuco, Mexico, 1022.
Barium, existence of, in all rocks of the primary formation, 444.
—— preparation of, from barium amalgam, 691.
—— bromide, action of chlorine on, 770.
—— —— action of oxygen on, 770.
—— chloride, action of oxygen on, 770.
—— chromate, crystalline, 437.
—— —— green pigment from, 987.
—— ethionate, 777.
—— ethylsulphate, action of ammonium sulphate on, 137.
—— ferricyanide, 702.
—— glycyrrhizate, 727.
—— hydrate, action of chlorine on, 505.
—— sulphate, estimation of, without filtering, washing, and drying, 480.
Barley, artificially manured, effect of, on the composition of the wort, 959.
—— Chili saltpetre as a manure for, 1051.
—— damage caused by sprouting in the field, 492.
—— effect of artificial manures on the growth of, 828.
—— seeds, influence of temperature on the evolution of carbonic anhydride by, 1048.
Basalts of the Auckland Islands, 903.
Base, $C_{19}H_{18}N_2$, new, 716.
Bases derived from aldol-ammonia, 704, 780.
Battery, Planté's, secondary, 101.
Bean insect, observations on the damage caused to Italian beans by, 552.
Beer analyses, 842.
—— Berlin, analysis of, 842.
—— detection of salicylic acid in, 343.
—— estimation of alcohol in, by means of the ebullioscope, 1065.
—— fermentation, 1079.
—— Hanoverian, analysis of, 843.
—— Munich, amount of phosphoric acid in, 843.
—— Nassau, analysis of, 843.
—— remarks on the estimation of calcium sulphate in, 79.
—— researches on, 1079.
—— standards of value for, 290.
—— worts, rotatory power of, 993.
—— yeast, composition of, 477.

Beer yeast, lecithin and nuclein in, 811.
—— —— pure, cultivation of, 1046.
—— —— researches on, 476.
Beeswax, adulteration of, 675.
—— crystalline, structure in, 171.
—— electrical properties of, 427.
—— testing of, for rosin, 283.
Beet cultivation, influence of time of manuring in, 825.
—— mucilage, 660.
—— ratio of sugar in, to the phosphoric acid in the root and leaves, 818.
—— leaves as fodder for cows, 813.
—— —— preservation of, 960.
Beetroot, choice of, for seed, 822.
—— cultivation, exhaustion of the soil by, 1050.
—— gum, composition of, 912.
—— nutritive value of seed-bearing, 822.
—— residues, distillation of, 913.
—— syrup, purification of, 844.
Beetroots, nitrates in, 337, 826.
Beet-sugar, influence of light on the yield of, 1047.
Beets, sugar, nitrates in, 826.
Benzal sulphide, 791.
—— —— action of potash on, 791.
Benzaldehyde nitro-, 152.
Benzaldehyde-green, 787.
—— —— metanitro-, 788.
—— —— metanitro-, reduction of, 788.
—— —— paranitro-, 788.
—— —— paranitro-, reduction of, 788.
—— —— reduction-products of, 787.
Benzaldiacetonamine and its salts, 54.
Benzamidotolylthiamide, 147.
Benzene, 571.
—— action of ethylene on, in presence of Al_2Cl_6, 785.
—— bromo-, acids produced by the introduction of, into the animal system, 796.
—— bromo-, action of, on the animal system, 803.
—— chloro-, acids produced by the introduction of, into the animal system, 796.
—— chlorodinitro-, action of hydrogen sulphide on, 230.
—— chlororthodinitro-, action of hydrogen sulphide on, 231.
—— compounds of aluminium chloride with, 308, 461.
—— —— diamylanhydrobenzyldiamido-, 923.
—— —— diethylanhydrobenzyldiamido-, 923.
—— derivatives, isomerism of, 380.
—— dinitrobromo-, 796.
—— *a*-dinitrochloro-, action of basic compounds on, 714.
Benzene, dinitrochloro-, reduction of, 376.
—— dinitroparadipropyl-, 142.
—— disulphoxide, 243.
—— exsiccator for, 875.
—— hexmethyl-, 527.
—— hydrocarbons produced by the action of methyl chloride on, in presence of aluminium chloride, 527.
—— hydrogenation of, 376.
—— monobromo-, action of sulphuric monochloride on, 229.
—— monochloro-, action of sulphuric monochloride on, 229.
—— nitrobromo-, 796.
—— nitro-metadichloro-, action of hydrogen sulphide on, 231.
—— nitro-paradichloro-, action of hydrogen sulphide on, 231.
—— nitrotribromo-, 800.
—— paradibromo-, 920.
—— paradipropyl-, and its derivatives, 142.
—— pentamethyl-, 527.
—— structural formulæ of di-, tri-, and tetra-chloro-, 526.
—— test for, 937.
—— tetrachloro-, 143, 144, 526.
—— trichloro-, action of copper on, 714.
—— trinitro-, addition compounds of, 50.
—— trinitroparadiphenyl-, 163.
—— and methyl chloride, hydrocarbons obtained by the action of aluminium chloride on, 228.
—— and petroleum spirit, characteristic differences between, 1063.
Benzenesulphamide, dibromo-, 797.
Benzenesulphanilide, nitration of, 922.
—— trinitro-, 922.
Benzenesulphinic acid, 915.
—— —— action of fuming nitric acid and of nitrous acid on, 314.
Benzenesulphone derivatives, melting points of substituted, 650.
Benzenesulphonic acid, amido-, 796.
—— —— and its salts, *a*-dihydroxy-, 933.
—— —— diazotetrabromo-, 802.
—— —— diazotribromo-, 801.
—— —— paradipropyl-, 142.
—— —— pentabromo-, and its salts, 802.
Benzenesulphonic acids, amidobromo-, and their salts, 796, 797.
—— —— bromo-, 796.
—— —— nitrobromo-, 796, 800.
Benzenesulphonic chloride, dibromo-, 797.
—— —— nitrotetrabromo-, 802.
—— —— nitrotribromo-, 800.
—— —— tetrabromo-, 801.
Benzenes, dinitroparadibromo-, and their derivatives, 50.

Benzenenaphthylamidine, 147.
Benzenyltolylamidotolylamidine, 147.
Benzenyltolyleneamidine, 147.
Benzhydrol, action of phosphorus pentasulphide on, 61.
—— nitration of, 319.
Benzhydrylpropioncarboxylic anhydride, 246.
Benzidine, 252.
—— diethoxy- (orthodiamidodiphenethole), 939.
—— —— action of alkalis on the salts of, 939.
—— preparation of, 630.
Benzimido-thiamyl ether, 147.
Benzimidothiobenzyl ether, 923.
Benzimidothioethyl ether, 922.
Benzoic acid, derivatives of, 246.
—— —— derivatives, heat of formation of, 873.
—— —— amido-, 151.
—— —— amido-, action of cyanogen on, 321.
—— —— amido-, heat evolved on combination of, with hydrochloric acid, 768.
—— —— cyanocarbimidamido-, 321.
—— —— anhydrorthosulphamine-, 628.
—— —— ε-diamido, 247.
—— —— dioxy-, 721.
—— —— hydroxy-, ether-sulphuric acids of, 150.
—— —— ε-hydroxynitro-, 246.
—— —— metaiodamido-, and its salts, 377.
—— —— metaiodonitro-, and its salts, 377.
—— —— metamido-, 381.
—— —— metanitro-, and barium salt of, 381.
—— —— α-metanitro-orthamido-, 381.
—— —— β-nitramido-, and its salts, 382.
—— —— ε-nitro-amido-, 246.
—— —— orthosulpho-, 629.
—— —— paranitro-, 631.
—— —— sulphoparachloro-, 155.
Benzoic acids, azo-, 152.
—— —— benzonitro-, 153.
—— —— α- and γ-hydroxynitro,- 247.
—— —— isomeric amido-, 154.
—— —— isomeric nitro-, 154.
—— —— mononitro-, 151.
—— —— nitro-, 150.
—— —— nitro-, lemon-yellow, 152.
Benzoic cyanide, 647.
—— —— action of phosphorus pentachloride on, 647.
Benzoïn, Siam, vanillin in, 245.
Benzonaphthylthiamine, 147.
Benzonitril, bromination of, 721.
—— chlorination of, 721.
Benzophenone, 318.
—— diacetoxy-, 326.
—— diacetyldiamido-, 319.
—— diamido-, 242.
—— β-diamido-, 319.
—— dibenzoxy-, 325.
—— diethoxy-, 325, 326.
—— dinitro-, 242.
—— α-, β-, and γ-dinitro-, 319.
—— dioxy-, 242, 326.
—— monethyldioxy-, 326.
—— monoxy-, formation of colouring matter from, 60.
—— nitration of, 319.
—— sulphuretted derivatives of, 61.
—— tetramethyldiamido-, 921.
—— thio-, 61.
Benzophenonedisulphonic acid, 318.
—— —— isomeric, 319.
Benzyl orthothioformate, 318.
Benzylamine and its salts, 921.
Benzylated cresol, 314.
Benzylic chloride, action of water on, 700.
Benzylcresotic acid, 315.
Benzyldiphenylamine, 147.
Benzylidenechloral ammonia, 452.
Benzylidenephthalyl, derivatives of, 246.
Benzylmalonic acid, 707.
Benzylmethylglycollic acid, 795.
—— —— action of sulphuric acid on, 795.
Benzylnaphthyl ketone, preparation of, 807.
Benzyl-phenylamine, 147.
Benzyl-phosphorus chloride, 721.
Berberine, 656.
Berberonic acid, and salts of, 656.
Bernadinite, a resinous mineral from California, 603.
Bessemer process, 566.
—— —— physical and chemical changes which specular iron undergoes when smelted in the cupola for, 840.
Beta vulgaris (*rubra*), colouring matter of, 730.
Betulin, 469.
—— hydrocarbon from, 469.
Bidara laut, 1045.
Bile, chemistry of, 949.
—— influence of, in digestion, 549.
—— ox-, preparation of glycocholic acid from, 949.
Bilic acid, new oxidation-products of cholic acid, 810.
—— —— oxidation of, 811.
Birds, secretion from the sebaceous glands of, 176.
Bismuth residues, 355.
—— subnitrate, presence of lead in, 80.

Bismuthine, 364.
Bitter almonds, essence of, chemical nature of, 719.
Black lac for metal and wood, 684.
—— pigment from iron scrap, 97.
Blast furnace, combustion in, 841.
—— furnaces, liquid cyanides and chlorides in, 989.
Bleaching powder, analysis of 505.
—— process for animal textile fibres, 99.
—— vegetable fabrics, 761.
Bletia Tankervillæ, indigo-blue from, 534.
Blood, action of amyl nitrite on, 816.
—— action of nitric oxide on, 817.
—— action of sodium nitrite on, 817.
—— arterial, tension of oxygen in, 811.
—— behaviour of potassium salts in, 816.
—— Bernard's method for the estimation of glucose in, 674.
—— distribution of phosphates in, 662.
—— estimation of glucose in, 557.
—— estimation of hæmoglobin in, 835.
—— estimation of oxygen in, 835.
—— estimation of sugar in, 674.
Blowpipe, use of, in quantitative analysis, 740.
Body colours, valuation of, 179.
Bohr's colorimetric process for the examination of water, 553.
Boiler feed-waters, analysis of, 273.
—— incrustation, composition of a, 839.
Boilers, heating steam, 1070.
Boiling and melting points of solid elements, thermo-chemical relation between, 690.
Boiling point determinations, apparatus for regulating the atmospheric pressure in, 346.
Bones, decomposition of, by steam, 987.
Boracetone, 915.
Borneo camphor, 1039.
Borneol, 1039.
—— bromide, 1040.
—— chloride, 1039.
—— isomerides of, 944.
Boron fluoride, action of, on acetone, 914.
—— glycide, 622.
—— mineral from Chili, 19.
Bottle glass, Macagno's investigations on, 562.
Boyle's law, deviation of some gases from, 346.
Bran, composition of the ashes of, 961.
Bravaisite, a new mineral, 442.
Bread, alum in, 556.
—— effect of alum on, 1077.
Breislakite, 206.
Brewing, analyses of water for, 1078.
Bromanilic acid, monochloromono-, 462.
Bromates, action of oxalic acid on, 593.
Bromides, anhydrous, metallic, action of chlorine on, 770.
Bromine, elimination of, from bromocitraconic acid, 1037.
—— estimation of, by ammonium thiocyanate, 973.
—— chlorine, and iodine, separation and estimation of, 670.
Bromisobutylformic acid, 140.
α-Bromisobutyric bromide, action of zinc-methyl on, 46.
—— —— normal, action of zinc-methyl on, 46.
Bromo-citraconic acid, elimination of bromine from, 1037.
Bromoform, action of alcoholic potash on, 126.
Bromonaphthalene, nitration of, 721.
Bromopropiolic acid, 225, 616.
α-Bromopropionic bromide, action of zinc-methyl on, 46.
Bromopurpureo-cobalt salts, 598.
Bromoterephthalic chloride, 639.
Brown hay, preparation of, from maize, 960.
Brown pigment from iron scrap, 97.
Brucine, absorption-spectra of, in solution, 269.
—— colour reaction with antimony trichloride, 832.
—— in *Bidara laut*, 1045.
Buchu, amount of ash and soluble matter in three kinds of, 391.
Bunsen's cells, treatment of, 576.
Butane, normal, action of bromine on, 302.
Butter analysis, 81.
—— Ghea- or Shea-, 568.
—— Hehner's method of testing, 181.
—— Marchand's method of determining, in milk, 675.
—— new method for detecting foreign fats in, 1069.
—— new method of testing, for foreign fats, 983.
—— simplification of Hehner's method of testing, 406.
—— testing of, 407.
—— fat, analysis of, 1070.
Butyl alcohol, normal, action of zinc chloride on, 1029.
Butylamine, di-, 141.
—— mono-, 141.
Butylchloral-ammonia, action of benzaldehyde on, 452.

Butylchloral hydrocyanide, 41.
Butylene, nitro-, 700.
—— nitro-, action of bromine on, 701.
—— nitro-, formation of, from butylene and nitric acid, 701.
—— nitro-, constitution of, 701.
—— pseudo-, 456.
Butyl-glyceric acid, 1032.
Butyl thiacetate, iso-, boiling point of, 786.
Butylthiocarbamide, tertiary, 713.
—— tertiary, 713.
Butyric acid, *a*-chloriso-, and some of its derivatives, 615.
—— —— chloroxy-, nitrile of, 449.
—— —— hydroxyiso-, 139.
Butyric leucine, 545.
Butyrofuronic acid, 916.

C.

Cabbage disease, 820.
Cacao, quantitative determination of theobromine in, 406.
Cacochlor, from Rengersdorf, 901.
Cacodylic acid, action of, on the animal organism, 476.
Cadmium, estimation of, 746.
—— electrolytic estimation of, 276, 746.
—— arsenates, 884.
—— bromide, vapour-density of, 875.
—— phosphide, 508.
Calcium bromide, action of oxygen on, 770.
—— chloride, 562.
—— chloride, action of oxygen on, 770.
—— glycerate, fermentation of, 664.
—— glycollate, crystallised, amount of water contained in, 522.
—— glycyrrhizate, 727.
—— lactate, fermentation of, 664.
—— malate, fermentation of, 664.
—— phosphate, deposits of, in the Vosges, 19.
—— saccharates, recovery of sugar from, 492.
—— sulphate, double salts of, 203.
—— —— —— in beer, remarks on the estimation of, 79.
—— sulphide, action of magnesium chloride on, 1012.
—— tartrate, fermentation of, 664.
Caliatour wood, colouring matter of, 470.
Calico, printing of, with cerium aniline-black, 683.
Californine, Winckler's, 73.
Calorimetric method, 586.
Calves, feeding, without the cows' milk, 1046.
Camellia japonica, investigation of the seeds of, 330.
Camellin, 330.
Camphene, 944.
—— a solid, 1039.
—— formula of, 167.
—— from camphor, 168.
—— ethyl-, 168.
—— isobutyl-, 168.
Camphic acid, transformation of, into camphor, 726.
Campholene, 540.
Camphor, 69.
—— Borneo, 1039.
—— cyano-derivatives of, 329.
—— dichloride, 168.
—— formula of, 167.
—— iodo-, 329.
—— transformation of camphic acid into, 726.
Camphoramic acid, action of dehydrating agents on, 539.
Camphoric acid, action of dehydrating agents on, 539.
Camphoterpene, 540.
Cancrinite, chemical composition of, 606.
Candle-nuts, composition of, 957.
Cane-sugar, specific rotatory power of, 136, 557.
—— and lime, action of, on mercurous chloride, 889.
Cane-sugars, crude, glucose in, 97.
Cantharene, 271, 655.
Cantharic acid and a hydrocarbon, C_8H_{12}, from, 270.
Cantharidin, derivatives of, and their relation to the ortho-series, 655.
Caoutchene, di-isoprene, and terpene, identity of the hydrates of, 1039.
Caoutchouc, analysis of, 559.
—— vulcanised, behaviour of, with illuminating gas, 188.
Capric acid, dibromo-, 521.
Caprylic acid and its salts, 1037.
Carbamide, dimethyl-, chloride of, 934.
—— dinaphthyl-, 723.
—— diphenyl-dimethyl-, 935.
—— methylphenyl-, chloride of, 935.
—— monochlorocrotonyl-, 41.
—— mononaphthyl-, 723.
—— naphthyl-, 723.
—— ortho-ditolyl-, 935.
—— orthophenylene-, 922.
—— phenyldimethyl-, 934.
—— tetramethyl-, 935.
—— tetranitrodiphenyl-, action of potash on, 67.
—— tetranitrodiphenyl-potassium, 67.
—— tetraphenyl-, 935.
—— amyl-, 913.
Carbamides, polysubstituted, 934, 935.

Carbinamine, trimethyl-, and its salts, 713.
Carbohydrate, new, 779.
Carbohydrates, behaviour of, towards chromates, under the influence of light, 911.
—— ethereal sulphates of, 1033.
—— of the Jerusalem artichoke, 778.
Carbon bisulphide, action of trimethylamine on, 304.
—— —— explosive product of a solution of phosphorus in, 996.
—— —— exsiccator for, 875.
—— —— manufacture in Swoszowice, 837.
—— —— use of, for the extraction of sulphur, 837.
Carbon, estimation of, in cast-iron, 401.
—— filters, experiments with, 986.
—— hydrogen, and nitrogen, simultaneous determination of, 278.
—— octobromide, 303.
—— separation of, in open hearth, puddling furnace, and Bessemer converts, 185.
—— a third form of, in steel, 842.
Carbonic acid, compound of alumina with, 885.
—— —— influence of temperature on excretion of, 74.
—— —— in the air, estimation of, 78.
—— —— replacing, of the air necessary for the production of chlorophyll in sarcophytic and parasitic plants, by organic substances, 737.
—— —— temperature-surface of, 195.
Carbonic anhydride, action of, on the animal organism, 174.
—— —— diffusion of, through water and alcohol, 347.
—— —— formation of, by yeast alone, in presence and absence of oxygen, 663.
—— —— influence of temperature on the evolution of, by barley seeds, 1048.
—— —— in sea-water, 1061.
—— —— preparation of, under any desired pressure, 676.
—— —— proportion of, in air, 744.
Carbonic oxide, action of aqueous vapour on, 880.
—— —— heat of combination with the elements, 591.
—— —— heat of formation of the compound of, with cuprous chloride, 888.
—— —— in foundry furnaces, 344.
—— —— limit of detection of, 1063.
—— —— solution of, in an acid solution of cuprous chloride, 887.
Carbopetrocene, 1027.
Carbotriphenyltriamine, synthesis of, 462.
Carboxypyridenic acid, 732.
Carica papaya, action of the sap of, 1048.
—— —— digestive ferment of, 1048.
Carminaphtha, Laurent's, 466.
Carrot seed, analysis of, 822.
Caryophyllaceæ, colouring matter of, 730.
Caseïn, 735.
—— formation of fat from, in the ripening of cheese, 996.
—— vegetable, 273.
Cast-iron, crystals extracted from, by ether or petroleum, 771.
—— —— estimation of carbon in, 401.
—— —— purification of, from phosphorus, 286.
Castor-oil seeds, albuminoïds from, 390.
Cat, respiration of a, 75.
Catalysis, 501.
—— viscosity a cause of, 876.
Catechu, test for, in tea, 854.
Catlinite, 361.
Cattle fodder, analyses of, 956.
Cellulose, action of gaseous hydrochloric, hydrobromic, hydriodic, or hydrofluoric acid on, 779.
—— nitro-derivatives of, 218, 371.
Cement, 407.
—— grinding apparatus for, 408.
—— influence of water on, 408.
Cereals, nitrogen-compounds present in, 486.
Cerite, analyses of, 682.
—— metals, estimation of, in scheelite, 696.
—— —— examination of calcareous minerals for, 696.
Cerium aniline black, 682.
—— chlorostannate, 602.
—— distribution of, 695.
—— group, new earth of, 12.
—— metals, specific gravity and atomic volume of, 579.
Charcoal, absorption of gases by a new series of equivalents or molecular numbers, 500.
—— animal, artificial, 844.
—— wood, absorbing power of, 761.
Cheese, decomposition of, 859.
—— formation of fat from caseïn in the ripening of, 996.
—— Parmesan, critical point in making, 764.
—— ripening of, 859.
Chemical affinity, 348, 580.
—— equivalence, 876.

Chemical technology of glass, 1074.
Chenopodium Quinoa, colouring matter of, 730.
Chestnut tree, disease of, 821.
Chicory, examination of, 558.
Chili saltpetre as a manure for barley, 1051.
Chinolic acid, action of nitric acid on, 947.
Chinoline-carbonic acid, 471.
—— constitution of, 946.
—— dichloro-, 946.
—— from allylaniline, synthesis of, 540.
—— nitro-, 540.
—— synthesis of, 946.
Chitenine, 809.
Chloral ammonia, action of aldehydes on, 452.
—— hydrate, 914.
—— —— dissociation of, 500, 690.
—— —— remarks on a note on, by Wurtz, 1006.
—— —— and chloroform, distillation of a mixture of, 876.
Chloralide and its derivatives, 43.
Chloranil, formation of, from isomeric amido-benzoic acids, 154.
Chlorates, action of oxalic acid on, 593.
Chlorides, liquid, in blast furnaces, 989.
—— metallic, vapour-densities of some, 1013.
Chlorine, action of, on anhydrous metallic bromides, 770.
—— acetate, Schützenberger's, 452.
—— bromine, and iodine, separation and estimation of, 670.
—— density of, at high temperatures, 1011.
—— estimation of, by ammonium thiocyanate, 973.
—— estimation of, in urine, 830.
—— preparation of, by means of calcium and magnesium chlorides, 8.
—— presence of, in scapolites, 697.
Chlorocrotonamide, 41.
Chloroform as an anæsthetic, 747.
—— detection of, 280.
—— exsiccator for, 875.
—— tests for the purity of, 747.
—— and chloral hydrate, distillation of a mixture of, 876.
Chloromuconic acid, 918.
Chlorophyll corpuscles, origin of, 174.
Chlorophyllite, gold and silver in, 511.
Chloropurpureo-chromium salts, 124.
Chloropurpureo-cobalt, salts of, 119, 124.
Chlorostannates of the rare metals, 601.
Chloroxindole chloride, 535.
Chocolate, quantitative determination of theobromine in, 406.
Cholamide, 949.
Cholanic acid and its salts, 388.
Cholesteric acid and its salts, 388.
Cholesterin, action of nitric acid on, 634.
—— brain, derivatives of, 135.
—— dinitro-, 634.
—— mononitro-, 634.
—— some neutral oxidation-products of, 135.
—— trioxy-, diacetin of, 135.
—— trioxy-, nitrous ether of, 135.
Cholesteryl chloride, action of aniline, toluidine, and naphthylamine on, 376.
—— —— action of nitric acid on, 634.
Cholesterylaniline, 135, 376.
Cholesteryl- α-naphthylamine, 376.
Cholesteryltoluidine, 376.
Cholic acid, 333, 949.
—— —— action of potassium dichromate and sulphuric acid on, 388.
—— —— a hydrocarbon from, 333.
—— —— oxidation of, 333, 810.
Chondrin, 661.
Chondroglucose, 661.
Chromates, 298.
—— behaviour of carbohydrates towards, under the influence of light, 911.
—— behaviour of gums towards, under the influence of light, 911.
—— detection of, 401.
—— of magnesium metals, volume-constitution of, 768.
Chromatic value of media other than water, 429.
Chrome-black on wool, 572.
Chrome-crucible steel, preparation of, 567.
Chrome steel, 286, 287.
Chromic acid, a new double salt of, 887.
—— —— compound of, with potassium fluoride, 1016.
—— —— free, detection of, 401.
Chromic compounds, absorption-spectra of, 190.
Chromium amalgam, 693.
—— compounds, inactivity of, in producing aniline-black as compared with the action of vanadium compounds, 421.
—— garnet, 361.
—— salts, action of, in presence of chlorates, 420.
—— and aluminium, sesquisulphates of, 595.
—— and iron, sesquisulphates of, 594.
—— and manganese, sesquisulphates of, 594.

Chromograph, 836.
Chromometry, use of blowpipe in quantitative analysis, 740.
Chronology of the isomeric purpurins, 943.
Chrysanisic acid, new method of preparing, 324.
Chrysarobin, acetyl-, 327.
—— in "Goa powder," 326.
Chrysazin, 538, 942.
—— constitution of, 942.
—— diacetyl-, 538.
—— from anthracene, synthesis of, 260.
—— series, anthracene-derivatives of, 537.
Chrysazol, 537.
—— diacetyl, 537.
Chrysene, colour reaction with antimony trichloride, 831.
—— synthesis of, 807.
Cinchomeronic acid, formation of, from quinine, 947.
—— —— identity of pyridinedicarbonic acid with, 947.
—— —— salts of, 947.
Cinchona alkaloïds, 168.
—— —— behaviour of potassium thiocyanate with, 281.
—— —— remarks on Rice's articles on, 71.
Cinchona barks, estimation of, 489.
—— —— exhibited at the Horticultural Exhibition in Amsterdam, estimation of the alkaloïds in, 281.
Cinchona bases, oxidation-products of, 656.
Cinchonichine, 169.
Cinchonidine, 71.
—— and its salts, 948.
—— oxidation of, 949.
Cinchonic acid, 947.
Cinchonine, 71, 655.
—— bases, constitution of, 810.
—— composition of, 948.
—— diethiodide, 169.
—— oxidation-products of, 471, 948.
—— reaction with antimony trichloride, 832.
—— solubility of, 489.
Cinchonine-quinoline, oxidation of, by potassium permanganate, 731.
Cinchotenicine, 332.
Cinchotenidine, 71.
—— and its salts, 949.
Cinchotenine, 948.
Cinchotine, 948.
—— or hydrocinchonine, 71.
Cinders from Etna, 904.
Cinnabar crystals from California, 440.
—— vapour-density of, 767.
Cinnamene, *a*-bromo-, 379.
Cinnamic acid, addition-products of, 378.
Cinnamic acid, hydriodo-, 378.
—— —— hydrobromo-, 378.
—— —— hydrodibromo-, 378.
—— —— metanitro-, 321.
—— —— metanitro-, synthesis of, 157.
Cinnamon-bark, Japanese, 320.
Citraconic acid, bromo-, 457.
Citramalic acid and its salts, 707.
Citrene, 386.
Clays, 988.
—— analysis of, 87.
Cleopatra's needle, analyses of stone, 445.
Clevite, 364.
Clover hay, action of rain on, 823.
Coal, artificial formation of, 896.
—— constitution of, 602.
—— dust, the part played by, in producing explosions in coal mines, 98.
—— estimation of sulphur in, 974.
—— mines, the part played by coal-dust in producing explosions in, 98.
Coal-tar, presence of ethyl alcohol in, 136.
Cobalt amalgam, 693.
—— ammonium compounds, 119, 438, 597.
—— complex oxides of, 507.
—— compounds, absorption-spectra of, 189.
—— estimation of, by precipitation as oxalate, 1054.
—— malleable, preparation of, and its application in the pure state, 563
—— metallurgy of, 285.
—— separation of ferric oxide and alumina from, 970.
—— and nickel sulphates, chemical equivalence of, 876.
Cocoa, nitrogenous constituents of, 493.
Codeine, colour reaction with antimony trichloride, 831.
—— test for, 1067.
Cœrulignone derivatives, 253.
Coffee, examination of, 558.
Cohesion, nature of, and its chemical signification, 579.
Cohesive power of soils, 957.
Coke, estimation of sulphur in, 974.
Collidine, 704.
Collieries, fire-damp in, 760.
Colloturine, 73.
Colombin, 730.
Colorimetric experiments, 77.
—— process (Bohr's) for the examination of water, 553.
Colostrum of the cow, composition of, 815.
Colour reactions, characteristic, produced by the action of antimony or bismuth trichloride on aromatic hydrocarbons, 831.

Colouring matter containing sulphur derived from dimethylphenylenediamine, 628.
—— —— from monoxybenzophenone, 60.
—— —— of *Palmella cruenta*, 1042.
—— —— of red wine, 171.
—— —— of sandal and caliatour woods, 470.
—— —— new, from orthamidophenol, 924.
—— —— yellow, from indigo, 936.
Colouring matters, 571.
—— —— from alizarin, absorption-spectrum of, 807.
—— —— of the rosaniline-group, 236.
Colours, valuation of body, 179.
Columbin and limonin, supposed identity of, 730.
Combustion-process, moist ; some reactions of alkaline permanganate of potassium, 555.
Concretion-balls, curious, derived from a colliery mineral water, 1024.
Conductivity of liquids for heat, 1001.
Conine, reaction with antimony trichloride, 831.
Conquinine sulphate, 656.
Copaibic acid, 1038.
Copper ammonium oxyferrocyanide, 775.
—— —— action of heat on, 775.
Copper, distribution of, in primordial rocks, and in the sedimentary deposits derived from them, 1020.
—— estimation and separation of, 971.
—— extraction of, by wet processes, 757.
—— improvements in purifying or refining, 423.
—— nitrite, a new, 693.
—— ores, origin of some, 17.
—— plate, steeling, 186.
—— phosphide, 504, 508.
—— refining, 989.
—— sulphate, absorption-spectra of, 190.
—— —— ammoniacal, action of potassium ferrocyanide on, 775.
—— sulphide, action of selenium on, 771.
—— —— precipitated, composition of, 206.
—— test, ammoniacal, and its application, 1066.
—— Weil's volumetric method of estimating, 276.
—— and iron pyrites, new processes for the treatment of, in the dry way, 563.
—— and lead, double selenides of, 440.
Corn, oiling of, 822.
Corpse, human, formation of poisonous alkaloïds in, 734.
Corundum in dolerite from Ovifak, 894.
Cotton-blue, 419.
Coumarin, homoacetoxy-, 720.
Cow, composition of the colostrum of, 815.
Cow-tree, composition of the milk of, 73.
Cows, beet-leaves as fodder for, 813.
—— use of sour food for, 1050.
Cows' milk, feeding calves without, 1046.
Cream, Devonshire, composition of, 1068.
Creasote, distinctive tests for, 182.
Creatine, 471.
Creatinine, 471.
Cresol, benzylated, 314.
—— distinctive tests for, 182.
—— para-, 789.
—— sulphuric acid, 149.
—— tetrabromopara-, 789.
Cresols, formation of, during putrefaction, 789.
—— three isomeric, action of carbon tetrachloride on, 791.
Crops, effect of manure on, 826.
Crossopterine, 71.
Croton aldehyde, action of ammonia on, 780.
—— —— and its homologues, 615.
Croton oil, volatile acid of, 221.
Crotonylamine, 712.
Crucible steel, manufacture of, 1076.
Cryohydrates, formation of, 428.
Crystal, preparation of large regular, 352.
—— species, fundamental forms of, 14.
Crystals extracted from cast-iron by ether or petroleum, 771.
Cumene, parabromo-, 624.
—— pseudo-, 623.
Cumenolcarbonic acid (propylhydroxybenzoic acid), 642.
Cumic acid, bromo-, 230.
—— —— dinitro-, 464.
—— —— nitro-, 464.
—— compounds, constitution of, 308.
Cuminol, nitro-, and its derivatives, 464.
Cupric hydrate, compounds of grape-sugar with, 778.
—— oxide (Fehling's solution), reduction of, by milk-sugar, 217.
Cuprosodiphosphonium chloride, 503.
Cuprous chloride, 693.
—— —— compounds of hydrogen phosphide with, 503.
—— —— heat of formation of the compound of carbonic oxide with, 888.
—— —— solution of carbonic oxide in an acid solution of, 887.

Cuprous chloride, vapour-density of, 767, 875.
—— thiosulphate, double salts of, 124.
Cyamides, action of carbonic anhydride on, 303.
Cyamidocarbonic acid, 304.
Cyanacetyldimethyl urea, 619.
Cyanacetyl urea, 619.
Cyanamide, phenyl-, preparation of, from monophenylthiocarbamide, 804.
—— reactions of, 910.
Cyanides, liquid, in blast furnaces, 989.
—— titration of, and relation to alkalimetry, 486.
Cyanogen, action of hydrochloric acid and alcohol on, 47.
—— direct combination of, with hydrogen, 909.
—— direct combination of, with the metals, 909.
—— estimation of, in soda-lyes, 402.
—— heat of formation of, 767.
—— hydride, solid, 1028.
Cyanuric acid, α- and β-, 517.
—— —— isomerides of, 517.
Cyclamin, splitting up of, into glucose and mannite, 70.
Cymene, β-chloro-, from thymol, 230.
—— compounds of, with aluminium bromide, 785.
—— compounds of, with aluminium chloride, 785.
—— constitution of, 308.
—— constitution of the propyl group in, 228.
—— oxidation of, 321.

D.

Dairy process, Alpine, 857.
Dandelion, analysis of, 821.
Daphnetin, 469.
—— benzoyl-, 469.
—— monacetyl-, 469.
—— tetrabromacetyl-, 469.
Dart, water from the, 906.
Daubréelite, the new meteoric mineral, 33.
Decipium, a new metal from samarskite, 117.
Decomposition, influence of chloroform in preventing, 395.
Dehydromucic acid and its salts, 141.
Deoxalic acid, 619.
Deoxybenzoïn, action of nitric acid on, 150.
—— amido-derivatives of, 790.
—— monamido-, chloroplatinate of, 791.
—— mononitro-, 790.
Deoxybenzoïn, nitro-derivatives of, 790.
—— synthesis of, 790.
Dephosphorisation of pig-iron, 1075.
Detonating agents, history of, 846.
Detonation, suddenness of, as compared with explosion, 847.
Dextran, 912.
Dextrose, estimation of, in presence of saccharose, 180.
—— gravimetric estimation of, 180.
—— -monochloride-tetrasulphuric acid, 1034.
—— -tetrasulphuric acid and its salts, 1034.
—— -trisulphuric acid, 1034.
Dhurra or Sorgho grass, cultivation of, 823.
Diabase from Berneck, 443.
Diallagite, 514.
Diallylacetic acid, 372.
Diallyl, monochloro-, 34.
Diallylene, 34.
Diallylisopropyl carbinol, 612.
Dialuric acid (oxymalonyl urea), 460.
Dialysis, apparatus for continual, 347.
Diamido-ditolyls (tolidines), isomeric, 235.
Diamines, homologous tertiary, obtained in the methylaniline manufacture, 786.
Diamylamine, preparation of, 914.
Diamylcarbopyrrolamide, 525.
Diamylene, heat of formation of, 874.
—— thermic constants of, 874.
Diaspore from Jordansmühl, 603.
Diastase, 660.
Diazobenzene-amidonaphthol, 629.
—— phenol-di-, 148.
Diazo-compounds, preparation of sulphonic compounds from, by means of sulphurous acid, 933.
Diazoethoxane, 221.
Diazohydrocyanorosaniline, 386.
Diazoleucaniline, 386.
Diazoparaleucaniline, chloride of, 385.
Diazopararosaniline hydrochloride, 385.
Diazorosaniline hydrochloride, 385.
Dibenzanilides, 716.
Dibenzoquinol, 638.
Dibenzoquinone dibenzoate, preparation of, 638.
Dibenzyl, perchlorination of, 721.
Dibenzylidene-amidobenzoic acid and salts of, 233.
Dibromallyl alcohol, action of chlorocarbonic ether on, in presence of sodium amalgam, 305.
Dibutylamine, 141.
Dibutyllactic acid, 616.
Dicarbopyridenic acid, 731.
—— —— action of heat on, 731.
—— acids, 265.

Dicarbopyridenic acids and their salts, comparative tables of the properties of, 267.
Dichlorhydrin, action of chlorocarbonic ether on, in presence of sodium amalgam, 305.
Dichloronaphthalene-β-sulphonic acid and its salts, 722, 723.
Dichlorosulphobenzide, 229.
Dichromates, 298.
Dickinsonite, 891.
Dicyano-amidobenzoyl, 321.
—— —— formula of, 466.
Dicyanodiamine, sulphuretted, 41.
Didymiferous minerals, measurement of absorption-spectra of, 697.
—— scheelite, artificial production of, 696.
Didymium chlorostannate, 602.
—— distribution of, 695.
—— from cerite, probable compound nature of, 119.
—— nitrate, spectrum of, 861.
—— oxide, pure, preparation of, 696.
—— tungstate, crystallised, preparation of, 696.
Diethylallyl carbinol, 214.
Diethyl-benzene, 785.
—— para-, 920.
—— -monosulphonic acid, 920.
Diethylbenzoic acid, Fittig and König's, 920.
Diethyl-carbopyrrolamide, 525.
Diethyl-glyoxylamide, 47, 220.
Diethylhydrazine, 450, 451.
Diethylnaphthylphosphine, 68.
Diethyloxamide, action of phosphorus pentachloride on, 784.
Diethyl sulphide, oxidation-products of, 37.
Dietrichite, a new alum from Hungary, 440.
Diffusion, use of, in the study of the phenomena of dissociation, 1006.
Digallic acid, 466, 646.
—— —— preparation of, 645.
Digestion, influence of bile in, 549.
—— pancreatic, 814.
Diguanidine and its salts, 781.
Dihydroferric phosphate, 202.
α-Dihydroxyanthracene, 537.
α-Dihydroxybenzenesulphonic acid and its salts, 933.
Di-isoamylsulphone, 38.
Di-isobutylamine, 703.
Di-isobutylglyoxylamide, 47.
Di-isobutyloxamide from commercial trimethylamine, 912.
Di-isobutylsulphone, 38.
Di-isobutylsulphoxide, 37.
Di-isoprene, caoutchene, and terpene, identity of the hydrates of, 1039.
Di-isopropylsulphone, 38.
Dimethacrylic acid, 307.
—— —— an isomeride of angelic acid, 782.
Dimethylamidotriphenylmethane, 53.
Dimethylamine, 913.
—— action of benzoic chloride on, 787.
—— preparation of blue colouring-matters from, 571.
Dimethylbarbituric acid, synthesis of, 618.
Dimethylcarbopyrrolamide, 525.
Dimethyldiacetonamine and its salts, 1035.
—— hydrochloride, 1035.
Dimethylethylcarbamine, 141.
Dimethylparaphenylene-diamine, 626.
—— —— action of ethyl-oxalate on, 627.
—— —— carbamides, 627.
—— —— colouring matter containing sulphur derived from, 628.
—— —— oxamic acid, 627.
—— —— -thiocarbamide, 628.
Dimethyluric acid, 48.
Dinaphthylcarbamide, 723.
Dinaphthyl-phosphinic acid, 67, 68.
Dinaphthyls, three, colour reaction with antimony trichloride, 831.
—— —— reaction with bismuth trichloride, 831.
—— vapour-densities of the three isomeric, 537.
Dinitrophenylpropionic acid, 640.
Diopside, 442.
—— artificial, formed in a Bessemer converter, 513.
Dioptase on chrysocolla, from Peru, 30.
Diortho-diphenylene-acetylene or phenanthrene, 653.
Dioxyanthracene, 258.
—— diacetyl-, 258.
—— dibenzoyl-, 258.
Dioxyanthrarufin, diacetyl-, 258.
Dioxybenzene, ether-sulphuric acids of, 149.
Dioxybenzoic acids, 157, 644.
Dioxybenzophenone, from aurin, 59.
Dioxyindole, acetyl-, 937.
—— action of ammonia on, 718.
Diparamidodimethylphenyl-oxamide, 627.
Diparamido-diorthocarboxyldiphenyl, or diamidodiphenic acid, 653.
Diphenethole, orthodiamido- (diethoxybenzidine), 939.
—— —— action of alkalis on the salts of, 939.
Diphenic acid, 165.
—— —— diamido-, or diparamido-diorthocarboxyldiphenyl, 165, 653.

Diphenic acid, dimetamido-, 653.
—— —— dinitro-, 165.
Diphenols, 64, 66, 651.
a-Diphenol-sulphonic acid, 65.
Diphenyl, colour reaction with antimony trichloride, 831.
—— colour reaction with bismuth trichloride, 831.
—— diamido-, 252, 652.
—— dibrom-hexmethoxyl, 253.
—— dichlorohexmethoxyl-, 253.
—— diphthalimido-, 324.
—— diphthalimidodibromo-, 324.
—— hexhydroxy-, 932.
—— hexmethoxy-, 253.
Diphenylamine, dinitro-, 51.
Diphenyl-arsenious acid, 162.
—— —— bromide, 162.
—— —— chloride, 162.
—— —— oxide, 162.
—— —— oxychloride, 162.
—— —— trichloride, 162.
Diphenylarsinic acid, action of, on animals, 476.
Diphenyl bases, 252.
Diphenylbenzene, 66.
—— perchlorination of, 721.
—— trinitropara-, 163.
Diphenylcarbamide, 651.
Diphenylcarbonic acid, 163.
Diphenyl-diethyl-arsenium iodide, 162.
Diphenylethylethane, 318.
Diphenylene-ketone, 164, 165, 166, 167, 536.
Diphenylene-ketone-carbonic acid, 166.
Diphenylene-methane, 164, 166.
—— —— dibromo-, 164.
—— —— dinitro-, 164.
—— —— picrate, 164.
Diphenylenephenylmethane, 384.
Diphenyl-ethylarsine, 162.
Diphenylmethane, nitration of, 319.
—— diacetoxy-, 325.
—— diamido-, 319.
—— dibenzoxy-, 325.
—— diethoxy-, 325.
—— dimethoxy-, 325.
—— dioxy-, 324.
—— —— oxidation of, 325.
—— —— tetrabromo-, 325.
Diphenylmethylacetic acid, 322.
Diphenylmethylmethane, 317.
Diphenylphthalide (phthalophenone), conversion of, into phenolphthaleïn, 637.
—— constitution of, 636.
Diphenylthiocarbamide, 54.
—— action of potassium monochloracetate on, 651.
Diphenylthiohydantoïn, 651.
Dipicoline and its salts, 265.
Dipyrocatechol, 65.
Dipropylallylcarbinol, preparation of, 136.
Dipropyloxamide from commercial trimethylamine, 912.
Dipyridine, 264.
Diresorcinol, tetrabromo-, 465.
Dissociation, use of diffusion in the study of the phenomena of, 1006.
Disthene from Central Africa, 24.
Distillation of a heterogeneous liquid, 875.
Distilleries of molasses, artificial yeast for, 1078.
Dita bark (*Alstonia* or *Echites scholaris*), basic constituent of, 332.
Ditaïne, 332.
Ditamine, 71.
Dithiodidimethylaniline, desulphurisation of, 714.
Ditolyl, perchlorination of, 721.
Ditolylsuccinimides, 528.
Di-triferric phosphates, 202.
Divaleryl, preparation of, 520.
Dolerite from Ovifak, minerals occurring with the metallic iron in, 894.
—— which encloses native iron of Greenland, 892.
Dolomite, yellow, from Bleiberg, 19.
Dracylic acid, amido-, 155.
Dulcitan, 1034.
Dulcitanpentasulphonic acid, 1034.
Dulcite, action of phosphorus pentachloride on, 917.
Duporthite, a new asbestiform mineral, 24.
Durene, 527.
—— derivatives (*a*-tetramethylbenzene) 713.
Durenyl, 714.
Durenyl-dibenzoyl, 713.
Durenyl-dicarbonyl-diphenyl, 713.
Duryl, 713.
Dyes of the rosaniline group, 787.
Dyeing with aniline-black, 684.
—— wool, use of chrome-alum in, 185.
Dystropodextrin, 549.

E.

Earth, a new, of the cerium group, 12.
Earth-metals, fluorescence of the salts of, 862.
Ebullioscope, 1065.
Echitamine, 71.
Edible-clay, 89.
Egg, fowl's, researches on the chemical changes occurring in, during incubation, 474.
—— "starch granules" and "amyloids" of, 662.

Egg, yolk of, ferment produced by the morbid growth of the bioplasm of, 478.
Eikosylene, a derivative of brown-coal paraffin, 699.
—— a derivative of lignite paraffin, 447.
—— chlorination of, 699.
Ekdemite, 22.
Elaterite, 301.
Electric conductivity of zinc sulphate solution, 864.
—— —— and thermo-electric position of steel in their relation to its hardness, 999.
—— currents, behaviour of, in rarefied gases, 345.
—— —— produced by the flow of liquids through tubes, 346.
—— discharge, silent, 435.
—— spark, continuous spectrum of, 765.
—— —— thermic and galvanometric laws of, 576.
Electricity, atmospheric, influence of, on plants, 818.
—— excitation of, by the contact of solid and gaseous bodies, 345.
—— quantity of, necessary for charging a platinum water-cell, 194.
—— static, distillation of liquids under the influence of, 997.
Electro-chemical actions under pressure, 293.
Electrolytes are salts, 1.
Electrolytic conduction, unipolar, 194.
Electrolysis of hydrogen peroxide, 878.
—— used in copper metallurgy, 760.
Electromotive force produced by the flow of liquids through tubes, 998.
—— power of gas elements, 998.
—— —— of a Grove's element in terms of Siemens-Weber units, 998.
Elements and their compounds, spectra of, 685.
—— relation between the melting points of, and their coefficients of expansion by heat, 588.
—— solid, thermo-chemical relation between the boiling and melting points of, 690.
Elemi-resin, reduction-products of, 69.
Ellagic acid, 930.
—— —— action of potash on, 932.
—— —— constitutional formulæ for, 932.
Emulsion, formation of, 549.
Enamel for cast iron, 755.
—— for wrought iron, 755.
Enstatite from South Africa, 513.
—— in the olivine nodules of the Gröditzberg, 514.
Eosin, manufacture of, 292.
Eosphorite, 20.
Epichlorhydrin, action of ammonia on, 1031.
—— action of chlorocarbonic ether on, in presence of sodium-amalgam, 305.
—— action of hydrocyanic acid on, 449.
—— action of potassium cyanate on, 217.
—— action of sodium on, 1031.
Epsomite, natural crystals of, of large size, 358.
Equivalence, chemical, 876.
Equivalents, new series of, from absorption of gases by charcoal, 500.
Erbium nitrate, spectrum of, 862.
Ergot, alkaloïds of, 387.
—— contribution to a knowledge of the alkaloïds of, 269.
Ergotinine, preparation of, 387.
Ericaceæ, ethereal oils of some, 641.
Erythrol, action of phosphorus pentachloride on, 917.
—— fermentation of, 664.
—— tetrasulphuric acid, and its salts, 1033.
Etch-figures on quartz-crystals, 439.
—— —— produced on the alums, 439.
Ethane, action of bromine on, 302.
—— chlorobrom-, nomenclature and boiling points of, 368.
—— dinitro-chlor-, 700.
—— halogen derivatives of, 212, 368.
Ethanes, normal (paraffins), boiling points of, 765.
Ethenyl-bicarbonic acid, 707.
—— ether, 707.
Ethenyldiphenylamidine, 313, 786.
Ethenyltolylamidine, 146.
Ether, exsiccator for, 875.
Ether-sulphuric acids of dioxybenzene, 149.
Ethereal oils of some Ericaceæ, 641.
—— sulphates of polyhydric alcohols and carbohydrates, 1033.
Etherification, chemical experiments on, 866.
—— influence of metallic chlorides on, 418.
—— thermal experiments on, 866, 870.
Ethers of α-dinitrophenol from α-dinitro-chlorobenzene, preparation of, 716.
—— of trinitrophenol, 923.
Ethionic acid, 777.
Ethyl acetate, action of mineral acids on the formation of, 870.
—— —— bromo-derivatives of, 137.
—— —— heat of formation of, 870.
—— alcohol, action of bleaching powder on, 910.
—— —— action of, on ethyl chlorosulphonate, 776, 777.

Ethyl alcohol, action of potassium diiodide on, 595.
—— —— action of potassium permanganate on, 205.
—— —— action of zinc chloride on, 1029.
—— —— presence of, in coal-tar, 136.
—— amido-acetate, 621.
—— anthrol ether, 654.
—— azobenzoates, 152.
—— benzoate, vapour-density of, 1025.
—— benzonitrobenzoate, 153.
—— benzylmalonate, 707.
—— brom-acetates, decomposition of, 220.
—— bromide, preparation of, 127.
—— bromisovalerate, action of sodium ethylate on, 706.
—— butyrates, boiling points of, 522.
—— chloride, heat of formation of, 870.
—— α-chlorisobutyrate, 615.
—— chlorocarbonate, action of, on diamylamine, 913.
—— —— action of, on monoamylamine, 913.
—— chlorosulphonate, action of ethyl alcohol on, 776, 777.
—— cholate, 949.
—— dehydromucate, 141.
—— deoxalate, two isomeric modifications, 620.
—— diamylcarbamate, 914.
—— dibenzoylphenylglycerate, 645.
—— diethomalonate, 707.
—— diphenate, 165.
—— disulphoxide, decomposition of, by potash, 219.
—— ethomalonate, 707.
—— formyltricarbonate, 918.
—— glycollates, boiling points of, 522.
—— hydrogen sulphate, 776.
—— isosuccinate, 783.
—— lactates, boiling points of, 522.
—— malonate, 707.
—— mercaptan, action of diazo-compounds on, 304.
—— methoxybutyrate, 523.
—— methylaceto-acetate, action of hydrochloric acid on, 706.
—— —— —— action of hydrocyanic acid on, 706.
—— monamyl-carbamate, 913.
—— monobrom- and dibrom-acetates, 138.
—— monochloraceto - acetate, compounds of, with metals, 915.
—— monochlorangelactate, 42.
—— nitro-acetate, 621.
—— α-nitro-mesitylenate, 156.
—— β-nitro-mesitylenate, 156.
—— oxalate, action of phosphorus pentachloride on, 138.
Ethyl oxyisobutylformate, 140.
—— parahydroxymesitylenate, 643.
—— phenylbenzoate, 164.
—— pyrotartrate, 134.
—— silicate, heat of vaporisation of, 767.
—— —— specific heat of, 767.
—— —— thermic researches on, 767.
—— sulphate, preparation of, 775.
—— sulphates, decomposition of, by gaseous hydrochloric acid, 137.
—— tetracetyl quinate, 159.
—— thiacetate, boiling point of, 786.
—— trichloracetate, 139.
—— trichloroxyvalerate, 42.
—— tropate, 720.
Ethylamine, formation of, 219.
Ethylamines, separation of, 305.
Ethylbenzene, 785.
Ethylbenzoic acid, mononitropara-, and its salts, 920.
Ethylcarbopyrrolic acid, 525.
Ethyldiacetic acid, detection of, in urine, 560.
Ethyldicarbopyrrolic acid, 525.
Ethyldiethyl glyoxylate, 46, 220.
Ethylene, action of chlorine monoxide on, 303.
—— action of hypochlorous acid on, 446.
—— action of, on benzene, in presence of Al_2Cl_6, 785.
—— action of oxidising agents on, 907.
—— bromide, action of water on, 700.
—— chloride, action of nitric acid on, 700.
—— chlorobrom-, nomenclature and boiling points of, 368.
—— dibrom-, ketone from, 220.
—— dibromide, thermic constants for, 435.
—— fluobor-, 915.
—— halogen derivatives of, 212.
Ethylenediethylsulphone, 39.
Ethylenedisulphuric acid and its salts, 712.
Ethylidene chloride, action of nitric acid on, 700.
—— chlorobromide, 369.
—— disulphuric acid and its salts, 710.
Ethylnaphthylamidine, 147.
Ethyl-nitrogen chloride, boiling point of, 781.
Ethyloxalic bromide, 139.
Ethyloxalic chloride, 139.
Ethylphenyl ketone, 529.
Ethylpyrrol, 525.
Eucrasite, a new mineral from Brevig, 31.
Eugenol, mercurdimethyl-, 790.

Eugenol, methyl-, derivatives of, 790.
—— monobromomethyl-, 790.
Eugenyl dibromide, monobromomethyl-, 790.
Eugetic acid, methyl-, 790.
—— —— —— action of potassium permanganate on, 790.
Eupitton, 253.
Eurotin, 415.
Evodia glauca, 333.
Expansion of solid and fluid bodies, 1002.
Explosion, suddenness of detonation as compared with, 847.
—— of nitromannite, 1080.
—— of the flour mills at Minneapolis, Minnesota, 1079.
Explosive compounds, improvements in the manufacture of certain, 422.
—— mixtures of air with combustible powders, 412.
—— product of a solution of phosphorus in carbon bisulphide, 996.
Eye, behaviour of the albumin of the refracting media of the, 834.

F.

Fabrics, vegetable, process for bleaching, 761.
Fairfieldite, 892.
Fassaite, 364.
Fat of butter, analysis of, 1070.
—— decomposition of, can be increased by reflex action, 76.
—— formation of, from caseïn in the ripening of cheese, 996.
—— in oil-seeds, advantages of only partially removing, 99.
—— milk-, quantitative estimation of, 1068.
Fats, foreign, in butter, new method for detecting, 1069.
—— —— new method of testing butter for, 983.
Fatty bodies, neutral, acids obtained by distilling the crude acids derived from the saponification of, in a current of superheated steam, 1036.
—— matters, estimation of, in feeding-stuffs, 558.
Feeding experiments with sheep, 951.
Feeding-stuffs, estimation of fatty matters in, 558.
Felspars, production of, by fusion, and by prolonged maintenance at a temperature near that of fusion, 358.
Ferment, a new organised, 817.
—— digestive, of *Carica papaya*, 1048.
Ferment of sour wine, action of, on good wine, 817.
—— produced by the morbid growth of the bioplasm of the yolk of egg, 478.
—— soluble alcoholic, non-existence of, 1046.
Fermentation, 663.
—— alcoholic, influence of oxygen on, 735.
—— beer, 1079.
—— lactic, conditions of, 663.
—— of albumin, 664.
—— of calcium glycerate, 664.
—— of calcium lactate, 664.
—— of calcium malate, 664.
—— of calcium tartrate, 664.
—— of erythrol, 664.
—— of gelatin, 664.
—— of glycerol, 664.
—— of hydroxyvaleric acid, 782.
—— of must, 993.
—— schizomycetic, 664.
Fermentations, fungoïd, 172.
Ferri et quinæ citras, B.P., estimation of quinine in, 405.
Ferric chloride as a purifier of water, 1072.
—— —— vapour-density of, 1014.
—— hydrate, estimation of, without filtering, washing, and drying, 480.
—— salts, dissociation of dissolved, 348.
—— —— reaction of salicylic acid with, 748.
—— and aluminium oxides, new method for separating, from manganese, 1055.
—— oxide and alumina, separation of, from manganese, zinc, cobalt, and nickel, 970.
Ferricyanides, 702.
Ferrochrome, 286, 287.
Ferrocyanides, metallic, law peculiar to, 830.
Ferro-manganese alloys, distribution of manganese in, 286.
Ferrosoferric sulphate, 104.
Ferrous dihydric phosphate, 201.
—— oxide, estimation of, in silicates, 484.
Ferruginous particles deposited by a sirocco at certain places in Italy, 515.
Fibrin, estimation of, 835.
—— ferment, preparation of, 474.
—— peptone, action of acetic anhydride on, 950.
Fibrous materials, 859.
Field crops, quantity of nitrogen which must be supplied to cultivated plants to ensure their normal development as, 668.

Filters, experiments with animal charcoal, silicated carbon, and spongy iron, 986.
—— silicated carbon and spongy iron, 493.
Fire, extinguishing, in tar distilleries, 1080.
Fire-damp, detection of, 991.
—— in collieries, 760.
Fish guano, estimation of phosphoric acid in, 968.
Flame, blue, from common salt, 497.
Flavopurpurin, 384.
—— anthrapurpurin and isopurpurin, actual relations of, 943.
Flour, alum in, 556.
—— detection and estimation of alum in, 483.
—— detection of alum in, by the logwood test, 483.
—— detection of blighted wheat in, by the spectroscope, 977.
—— method for rapidly incinerating, 282.
—— mills at Minneapolis, Minnesota, explosion of, 1079.
Fluobenzenesulphamide, para-, 650.
Fluobenzenesulphochloride, para-, 649.
Fluobenzenesulphonic acid, 649.
Fluoboracetone, 914.
Fluoborethylene, 915.
Fluoranthene, a new hydrocarbon from coal-tar, 165.
—— constitution of, 536.
—— dibromo-, 166.
—— picric acid, 166.
—— quinone, 166.
—— trinitro-, 166.
Fluorene, diamido-, 653.
Fluoresceïn, manufacture of, 292.
—— nitroso-compounds of, 383.
—— carbonic acid, 55.
—— —— acetyl, 56.
—— —— dibromo-, 56.
—— —— tetrabromo-, 56.
Fluorescence of the salts of the earth-metals, 862.
—— Stokes's law of, 862.
Fluorine, volumetric estimation of, 829.
Fluorite (fluor-spar), from Evigtok in Greenland, 511.
Fluor-spar (fluorite), from Evigtok in Greenland, 511.
Fodder, cattle, analyses of, 956.
—— for cows, beet-leaves as, 813.
—— green, preservation of, in pits, 1049.
Fodders, analysis of some, 552.
Food, sour, use of, for cows, 1050.
Force, electromotive, produced by the flow of liquids through tubes, 998.
Formic acid, tribasic, ethereal salts of, 453.
Formyltricarbonic acid, 707.
—— ether, 707.
Fossilised wood in Cleveland ironstone, 91.
Fossil resin, sulphur in, 896.
Fowls poisoned with pumpkin-seeds, 1046.
Fowl's egg, researches on the chemical changes occurring in, during incubation, 474.
Freezing mixture of calcium chloride and snow, 689.
Fuel, new application of rapid oxidation by which sulphides are utilised for, 755.
—— used in the iron industry, estimation of sulphur in, 974.
Fürstenwald-glaze, 88.
Fulminoplatinum, chloroxy-, 375.
Fulminoplatinums, 373.
—— di-, tri-, and tetra-chloro-, 374.
Fumaric acid, 372.
—— —— action of ethyl iodide on the silver salt of, 223.
Fungus, distribution of, 479.
Furfuraldehyde, occurrence of, in glacial acetic acid, 137.
Furfurangelic acid, conversion of, into azelaic acid, 915.
Furfurvaleric acid, 916.

G.

Gadolinite-earths, 113.
Galvanic current, passage of, through iron, 686.
—— deposits, pressures produced by, 576.
—— polarisation, 577.
—— properties of aqueous solutions of metallic salts, 863.
Ganomolite, 22.
Galactose, 137.
Gallic acid, melting point of, 160.
Gamboge, analysis of, 1041.
Gambogic acid, 1042.
Garnet chromium-, 361.
—— from the erratic gneiss of Wellen, near Bremen, 361.
—— magnesium-, or Russian retinite, 441.
Gas, composition of, from a shaft of Abercarn Colliery, 357.
—— elements, electromotive power of, 998.
—— evolved by the action of barium hydrate on albuminoïds, 735.
—— holder, a simple, 877.
—— illuminating, quantitative determination of sulphur in, 78.

Gas lighting, 85.
—— liquor, application of, to the production of potassium carbonate and other salts, 677.
—— —— testing and valuing, 79.
—— purification of, by ammonia, 986.
—— regulator for air-baths, 294.
—— the ammonia-soda process in conjunction with the manufacture of, 837.
Gases, absorption of, by charcoal. A new series of equivalents or molecular numbers, 500.
—— combustible, composition of, in the Stassfurt Mines, 603.
—— compressibility of, 429.
—— compressibility of, at high temperatures, 1004.
—— deviation of some, from Boyle's law, 346.
—— hot, erosive action of strongly compressed, with reference to the history of meteorites, 1024.
—— in iron and steel, 437.
—— influence of temperature and pressure on the spectra of, 101, 685.
—— magnetic rotatory power of, at ordinary temperature and pressure, 576.
—— new phenomena shown by, 587.
—— rarefied, behaviour of electric currents in, 345.
—— rarefied, luminous appearances of, in tubes with liquid electrodes, 861.
—— relation between the specific heat temperature and heat conductivity, 2.
—— relation between work effected by the diffusion of, and the second law of thermodynamics, 3.
—— thermal effect of the walls of closed vessels on the contained, 432.
Gay-Lussac and Thenard, peculiarity of an experiment of, 887.
Gedanite, a new fossil resin, 300, 896.
Gelatin, action of potassium or ammonium dichromate on, 911.
—— blasting, 850.
—— fermentation of, 664.
Gerland's process for tannin estimation, 933.
Germination, influence of salicylic acid, thymol, and some essential oils on, 172.
Ghea- or Shea-butter, 568.
Glass, bottle, Macagno's investigations on, 562.
—— chemical technology of, 1074.
—— coloured by gold, 509.
—— composition of, 754.
—— durability of, 754.
Glaze-clay, analysis of, 87.
Glucoproteïns, 545.
Glucose, Bernard's method for the estimation of, in blood, 674.
—— estimation of, in the blood, 557.
—— examination of Pavy's method of determining, 834.
—— in crude cane-sugars, 97.
Glucoses, consecutive alteration of, formed by the inversion of cane-sugar, 369.
Glucoside of buckthorn berries, 39.
—— of liquorice, 727.
Glutamic acid, 545.
Glutimic acid, 545.
Glycerin. See Glycerol.
Glycerol, action of potassium permanganate on, 205.
—— application of, in analysis, 178.
—— derivatives of, 1029.
—— estimation of, in wine, 404.
—— ether of α-dinitrophenol, 717.
—— fermentation of, 664.
—— mononitro-, 449.
—— thermic constants of, 874.
Glyceryl-trisulphuric acid, 1033.
Glycide, 449, 1032.
Glycocholic acid, preparation of, from ox-bile, 949.
Glycocine, formation of, from ethyl nitro-acetate, 621.
Glycocyamine, synthesis of, 70.
Glycogen, action of diastase, saliva, and pancreatic juice on, 370.
—— transformation of, by the salivary and pancreatic ferments, 548.
Glycol-disulphuric acid and its salts, 1033.
Glycollic acid, formation of, from tartaric acid, 916.
Glycuvic acid and salts of, 524.
Glycyrrhizate of ammonium, acid, 1040.
Glycyrrhizic acid and its salts, 1040.
Glycyrrhizin, 727, 1040.
Glyoxylic acid, 619.
—— —— action of aniline on, 51.
Glyoxilin, 850.
Gneiss of the North Eastern Schwartzwald, and its relationship to the mineral veins, 443.
—— red, of the Saxon Erzgebirge, 361.
"Goa powder," chrysarobin in, 326.
Gold and other metals, extraction of, from pyrites, 288.
—— assaying of, 509.
Goosefoot, white, analysis of, 821.
Gourd family, analyses of some species of, 961.
—— seeds, albuminoïds of, 272.
Grains from malt, composition of, 761.
Gramenite, 31.
Grammatite, 364.

Granatine, 170.
Granite porphyry of Beucha, near Leipzig, 27.
—— —— of Lower Silesia, 29.
Grape-sugar, arsenic in, 1077.
—— —— compounds of, with cupric hydrate, 778.
Grapes, composition of, at different stages of ripeness, 820.
—— influence of heat on the ripening of, 1047.
—— of the Stein and Leisten districts, analysis of, 739.
—— ripening of, 174.
Graphite in dolerite from Ovifak, 894.
Grass seeds, cultivation of, 823.
—— young, nitrogenous constituents of, 819.
Green, a new fast (malachite green), 571.
—— aniline colours, 83.
—— fodder, preservation of, in pits, 1049.
—— pigment from barium chromate, 987.
Grossalmerode-clay, 89.
Grossular, 606.
Grove's element, electromotive power of, in terms of Siemens-Weber units, 998.
Guanidine, β-dicyanoditolylphenyl-, 53.
—— β-dicyanotriphenyl-, 53.
—— β-dicyanotritolyl-, 54.
—— diphenyl-, action of phenylthiocarbimide on, 804.
—— nitroso-, 613, 914.
—— salts of, 914.
—— thiocyanate, removal of sulphur from, 614.
Guanidines, cyano-, 53.
Guano, fish, estimation of phosphoric acid in, 968.
Gum, beetroot, composition of, 912.
Gums, behaviour of, towards chromates under the influence of light, 911.
Gun-cotton, decomposition of, in a closed vessel, 991.
Gunpowder, combustion of, 992.
—— observations on Noble and Abel's memoir on the combustion of, 875.
Gypsum, detection of, in meal, 183.

H.

Hæmocyanin from the blood of the *Octopus vulgaris*, 333.
Hæmoglobin, estimation of, in blood, 835.
Hair, conversion of, into manure, 859.
Halogens and oxygen, reciprocal displacements of, 351.
—— —— relative affinities of, 351.
—— sulphur, and oxygen, reciprocal displacements between the, when combined with hydrogen, 296.
Haloïd acids, decomposition of, by metals, 589.
—— ethers, formation of, in the gaseous state, 435.
Hay, brown, preparation of, from maize, 960.
—— clover, action of rain on, 823.
—— nitrogenous constituents of, 819.
—— preparation of quinic acid from, 952.
Heat absorbed by the solution of potassium chloride in water, 588.
—— action of, on copper-ammonium oxyferrocyanide, 775.
—— action of, on metals in a vacuum, 1018.
—— action of, on sugar, 911.
—— action of, on sugar solutions, 911.
—— atomic theory of, 687.
—— conductivity of liquids for, 1001.
—— developed by contact of water with anhydrous sodium sulphate, 589.
—— effect of, on mercury di-iodide, 498.
—— effect of substitutions, 871.
—— evolved by the action of hydrochloric acid on chloranilines, 872.
—— evolved by the action of hydrochloric acid on paranitraniline, 872.
—— evolved by the action of sodic oxide on the isomeric monochloranilines, 768.
—— evolved by the action of sodic oxide on the three isomeric nitrophenols, 768.
—— influence of, on the ripening of grapes, 1047.
—— influence of substitution on evolution of, during the formation of salts, 767.
—— invisible, refraction of, 864.
—— of formation of acetic derivatives, 872.
—— of formation of alkaline sulphides, 865.
—— of formation of aniline hydrochloride, 767.
—— of formation of benzoic acid derivatives, 873.
—— of formation of cyanogen, 767.
—— of formation of diamylene, 874.
—— of formation of dissolved alkaline sulphides, 866.
—— of formation of ethyl acetate, 870.

Heat of formation of ethyl chloride, 870.
—— of formation of hydrogen phosphides and arsenides, 5.
—— of formation of paranitraniline hydrochloride, 768.
—— of formation of phenol derivatives, 874.
—— of formation of silicon hydride, 767.
—— of formation of some aniline derivatives, 871.
—— of formation of the amalgams of the alkali metals, 884.
—— of formation of the compound of carbonic oxide with cuprous chloride, 888.
—— of formation of toluidine hydrochloride, 871.
—— of hydration of alkaline sulphides, 865.
—— of hydration of sodium oxide, 689.
—— of oxidation of the amalgams of the alkali metals, 884.
—— of solution of nitrates, sulphates, dithionates, and some other salts, 6.
—— of vaporisation of amylene, 874.
—— of vaporisation of ethyl silicate, 767.
—— of vaporisation of silicium chloride, 767.
—— specific, of uranoso-uranic oxide, 688.
—— capacity of mixtures of methyl alcohol and water, 688.
—— —— of soils, 958.
Heating steam boilers, 1070.
Heavy spar, detection of, in meal, 183.
Hectograph, 836.
Helicin or ortho-formyl glucoside, synthesis of, 1038.
Heliographic printing, 750.
—— —— on sheet-zinc, 751.
Hemp, strength of, 859.
Hepta-ammoniacal hydrochloride, 502.
Heptic acid, 458.
Heptyl alcohol, 46.
Herbivora, excretion of phosphoric acid by, 392.
Hesperidin sugar, 468.
Hessite, 898.
Hetaerolyte, a new mineral, 17.
Hexbromethylmethyl ketone, 220.
Hexmethylbenzene, 49, 527.
—— preparation of, from acetone, 940.
Hexhydroxydiphenyl ketone, 932.
—— —— carbonic anhydride, 933.
Hexane, action of bromine on, 303.
—— hexabrom-, 303.
—— octobrom-, 303.
Hexhydrohydiphenyl, 932.
Hexic acid, 457.
Hexmethyltriamidotriphenylmethane, 236.
Hexyl iodide, action of water on, 700.
β-Hexyl iodide, isoheptylic acid from, 140.
Hexylene, octobrom-, 303.
Hibernation, experiments on a marmot during, 75.
High temperature produced by means of ammonium nitrate, 102.
—— temperatures, spectrometric determination of, 293.
Hipparaffin, formula of, 650.
Hipparin, 650.
Hippuric acid, estimation of, 748.
—— —— separation of, 748.
—— —— source of, in the urine of herbivorous animals, 952.
Hisingerite in dolerite from Ovifak, 894.
Hollway's method of treating pyrites, 563, 755.
Homilite, 32.
Homocinchonidine-diethiodide, 169.
Homocinchonidine, ethyl-, 169.
Homo-oxybenzyl alcohols, xylenols, hydroxytoluic aldehydes and acids, alcohol- and aldehyde-hydroxybenzoic acids, and hydroxyphthalic acids, relation between, 924.
Homosalicylic acids, 530, 531.
—— —— three isomeric, 791.
Honey from Ethiopia, analysis of, 450.
Hops, analysis of, 957.
—— constitutents of, 171.
—— spent, analysis of, 1050.
Hornstone, a decomposition of, 511.
Horse-radish, mineral constituents of, 819.
House-fungus, prevention of, 1080.
—— —— salicylic acid as a preventative of, 1080.
Humic acid, 603.
Hunyadí Janos springs at Buda-Pest, analysis of, 366.
Hyalotekite, 22.
Hydratropic acid, 380.
—— —— amido-, 379.
—— —— dibrom-, 379.
Hydrazine compounds of the paraffin series, 450.
Hydrazobenzene, action of acetic anhydride on, 630.
—— diacetyl, 630.
Hydrazophenetols, 317.
Hydrindic acid, acetyl-, 937.
—— —— diamido-, 63.
Hydrindin-carboxylic acid, diamido-, 63.
Hydriodo-angelic acid, 618.
Hydriodo-methylcrotonic acid, 618.
Hydroanthracenehydroquinone, constitution of, 261.

Hydrobromic acid, absorption of, by acetic acid, 705.
Hydrocarbon, C_8H_{12}, from cantharic acid, 270.
—— $C_{14}H_{22}$, from lactucone, 469.
—— $C_{16}H_{12}$, from phenylglycol, derivatives of, 327.
—— from rosin oil, 467.
—— solid, occurrence of, in the eruptive rocks of New Jersey, U.S.A., 896.
Hydrocarbons, action of platinum wire on, 302.
—— aromatic, characteristic colour reactions produced by the action of antimony or bismuth trichloride on, 831.
—— from American petroleum, 447.
—— obtained by the action of aluminium chloride on methyl chloride and benzene, 228.
—— produced by the action of methyl chloride on benzene, in presence of aluminium chloride, 527.
—— unsaturated, action of nitrosyl chloride on, 517.
—— —— action of nitrous acid on, 35.
—— —— formation of, from the addition-products of non-saturated acids, 376.
—— —— resulting from the decomposition of American petroleum, 1025.
Hydrocarbostyril, amido-, 640.
—— dibromamido-, 640.
—— mono- and di- bromamido-, 640.
Hydrocele, nature of the albumins in, 550.
Hydrocellulose, 779.
—— conversion of, into pyroxylin, 911.
—— nitrification of, 911.
Hydrocerussite, 22.
Hydrochloric acid, absorption of, by acetic acid, 705.
—— —— compounds of the terpenes with, 943.
—— —— containing phosphoric acid, 8.
—— —— new compounds of, with ammonia, 501.
—— —— preparation of, by means of calcium and magnesium chlorides, 8.
—— —— solubility of stannic oxide in, 888.
—— —— gas, action of, on sulphates, 105.
—— —— —— and mercury, reaction between, 298.
Hydrocinchonine or Cinchotine.
Hydrocinnamic acid, formation of, by means of the pancreas ferment, 465.
—— —— amido- (phenylamidopropionic acid), 378.
Hydrocinnamic acid, amidonitro-, 640.
—— —— dinitro,- and its derivatives, 639.
—— —— paramethyl-, 230.
Hydrocyanic acid, 909.
—— —— action of hydrochloric acid and alcohol on, 46.
—— —— delicacy of some reactions for, 403.
—— —— estimation of, in bitter-almond water, 280.
—— —— titration of, and its relation to alkalimetry, 486.
Hydrogen, action of, on sodium oxide, 689.
—— atomic heat of, in its combination with palladium, 590.
—— direct combination of cyanogen with, 909.
—— estimation of, in gaseous mixtures, 670.
—— ignition point of, 587.
—— photographed spectrum of, 497.
—— and marsh-gas, fractional combustion of, 747.
—— carbon and nitrogen, simultaneous determination of, 278.
—— peroxide, 353, 592.
—— —— decomposition of, by cobalt, lead, and manganese oxides, 501.
—— —— electrolysis of, 878.
—— —— estimation of, by colorimetric method, 743.
—— —— estimation of, by hydriodic acid, 742.
—— —— estimation of, by indigo, 743.
—— —— estimation of, by measuring the oxygen evolved, 743.
—— —— estimation of, by permanganate, 740.
—— —— formation of, by the explosion of a mixture of oxygen and hydrogen, 103.
—— —— supposed existence of, in the organism of plants, 665.
—— phosphide, compounds of, with cuprous chloride, 503.
—— —— estimation of, in gaseous mixtures, 503.
—— phosphides and arsenides, heat developed in the formation of, 5.
—— sulphide, action of, on sulphurous acid in presence of salts, 1012.
—— —— preparation of, 1013.
—— —— use of, in the dry way in analysis, 963.
—— —— and sulphurous acid, production of sulphur from, 1012.
Hydrohæmatite of Neuenburg, 604.
Hydroisatin, constitution of, 937.
Hydroquinone. See Quinol.
Hydrotiglic acid and its salts, 456.

Hydrotiglic acid, brom-, 455.
—— —— dibrom-, 456.
Hydroxanic acid, 227, 461.
Hydroxy-acids, boiling points of ethereal salts of, 522.
Hydroxyanthraquinone-sulphonic acids, 255.
Hydroxybenzoic acid, meta-, aldehydhydroxybenzoic acids from, 927.
—— —— metahomopara-, 791.
—— —— nitro-, 644.
—— —— orthohomopara-, 791.
—— acids, alcohol- and aldehyde-, xylenols, homo-oxybenzyl alcohols, hydroxybenzoic aldehydes and acids, and hydroxyphthalic acids, relation between, 924.
—— —— aldehydo-, from metahydroxybenzoic acid, 927.
Hydroxybutyric acid, 615.
Hydroxycumic acid, 624.
Hydroxydiphenyls, three isomeric, 931, 932.
Hydroxyhydroanthranol, 261.
α-Hydroxyisophthalic acid, 795.
β-Hydroxyisophthalic acid, 793.
Hydroxylation by direct oxidation, 139.
Hydroxymesitylenic acid, a new, 643.
—— —— and its salts, 530.
—— —— constitution of, 530.
Hydroxyparaxylic acid, 641.
Hydroxyphthalic acids, oxidation of hydroxytoluic acids to, 791.
—— —— xylenols, homo-oxybenzyl alcohols, hydroxytoluic aldehydes and acids, and alcohol- and aldehyde-, hydroxybenzoic acids, relations between, 924.
Hydroxypropenylbenzoic acid, 465.
—— —— isomeride of, 466.
Hydroxypropylbenzoic acid, 465.
—— —— derivative of, 795.
—— —— oxidation-products of, 795.
Hydroxysalicylic acid, para-, 928.
Hydroxyterephthalic acid, 639, 793.
Hydroxytetric acid, 459.
Hydrotoluic acid, 530.
—— acids and aldehydes, xylenols, homo-oxybenzyl alcohols, alcohol-, and aldehyde- hydroxybenzoic acids, and hydroxyphthalic acids, 924.
—— —— from the three isomeric cresols, 791.
—— —— methylic salts of, 792.
—— —— oxidation of, to hydroxyphthalic acids, 791.
—— aldehydes and acids, xylenols, homo-oxybenzyl alcohols, alcohol- and aldehyde-, hydroxybenzoic acids, and hydroxyphthalic acids, relations between, 924.
Hydroxytrimesitic acid, 531.
Hydroxyuvitic acid, 531.
Hydroxyvaleric acid, obtained by oxidation of allyldimethyl carbinol, 618.
—— —— fermentation of, 782.
Hygrophilite-like mineral, 208.
Hypophosphoric acid and its salts, 105.
Hypoxanthine, 471.
—— occurrence and origin of, in the animal body, 170.

I.

Ibotin, 330.
Icacin, 73.
Idocrase in the limestone-strata of Deutsch-Tschammendorf, 902.
Idrialin, 167.
—— bromine-derivatives of, 167.
—— oxidation-products of, 167.
Imido-deoxybenzoincarbonic anhydride, 246.
Imidothio-ethers, 147.
Incrustation, boiler, composition of a, 839.
Indican, detection of, in urine, 343.
Indifulvin, 533.
Indigo, action of sodium thiosulphate on, 936.
—— amido-, 939.
—— brom-, 938.
—— constitution of, 806, 935.
—— molecular weight of, 532.
—— nitro-, 938.
—— reduction of, by glycerol, 188.
—— vapour-density of, 63.
—— yellow colouring matter from, 936.
Indigo-blue, 532, 535.
—— —— group, 937.
—— —— substitution-products, 938.
Indigofera tinctoria, indigo-blue from, 534.
Indigo-purpurin, 535.
—— —— brom-, 938.
—— —— nitro-, 939.
Indigotin, derivatives of, 936.
Indirubin, 533.
Indium chloride, vapour-density of, 579.
Indole, acetyl-, 938.
—— dioxy-, action of ammonia on, 718.
Indophenin, 937.
—— bromo-, 938.
Indoxyl, 806.
Indoxylsulphuric acid, 806.
Inorganic bodies, vapour-density determinations of, at high temperatures, 766.
—— compounds, vapour-densities of some, 875.
Insect powder, active principle of, 807.

Inulin, action of sulphuric monochloride on, 1035.
Iodated potassium iodide, 595.
Iodates, action of oxalic acid on, 593.
—— reduction of, by phosphorus, 103.
Iodine, absorption spectra of, 190.
—— estimation of, by ammonium thiocyanate, 973.
—— estimation of, in varec, 1051.
—— industry in France, 283.
—— reaction of, with sulphurous acid, 352.
—— acetate, Schützenberger's, 452.
—— chlorine, and bromine, separation and estimation of, 670.
—— sulphide (?), 353.
Iodine-green, 84.
Iodobromite, a new silver haloïd, 365.
Iodosalicylic acids, 928.
Iodosulphates of the quinine alkaloïds, 982.
Ions, transference of, 193.
Italian beans, observations on the damage caused by the bean insect, 552.
Iridio-platinum, alloy of, 774.
—— —— preparation of, 772.
Iridium, atomic weight of, 125.
—— dyad-, double salts of, 125.
—— pure, preparation of, 773.
Iron albuminates, 170.
—— amalgam, 693.
—— amidonitrosulphide, 597.
—— ancient, analysis of, 1074.
—— phosphorus in, 1074.
—— cast, crystals extracted from, by ether or petroleum, 771.
—— —— enamel for, 755.
—— finely-divided, magnetic behaviour of, 1000.
—— gases in, 437.
—— heated with phosphoric acid, 93.
—— industry, estimation of sulphur in the products of, 974
—— malleable, at the Paris Exhibition of 1878, 679.
—— manganiferous pig-, preparation of, 755.
—— manufacture, Blair's process for, 89.
—— meteoric nickeliferous, report on the researches of S. Meunier relative to, 905.
—— native carburetted, artificial production of, 693.
—— —— from Ovifak, 892.
—— —— of Greenland, 892.
—— —— of Greenland, origin of, 895.
—— ores, direct preparation of wrought iron and steel from, 409.
—— —— estimation of sulphur in, 974.
Iron, passage of the galvanic current through, 686.
—— phosphorus in, 90.
—— pyrophoric, 119.
—— pig-, dephosphorisation of, 1075.
—— plates, action of sea water on, 564.
—— red hot, action of the vapour of potassium or sodium hydrate on, 887.
—— reduced by hydrogen, 887.
—— remarkable specimen of silicon, 204.
—— salts in tea, detection of, 854.
—— —— reaction of salicylic acid with, 748.
—— smelting in the cupola furnace, 564.
—— specular, physical and chemical changes which it undergoes when smelted in the cupola for the Bessemer process, 840.
—— spongy, and animal charcoal as materials for purifying water, 343.
—— sulphate, a new variety of (luckite), 901.
—— sulphides, action of ether on, 771.
—— surface, new method of producing a coating of magnetic oxide on, 840.
—— white pig-, specific gravity of, 840.
—— wrought, direct preparation of from iron ores, 409.
—— —— direct process for making, 565.
—— —— enamel for, 755.
—— and alumina, acid sesquisulphate of, 594.
—— and chromium, sesquisulphates of, 594.
—— and copper pyrites, new process for the treatment of, in the dry way, 563.
—— and manganese, sesquisulphate of, 594.
—— and silver, sulphide of, from Andreasberg, 440.
Iron-glance, magnetic pseudomorph after, 363.
Ironstone, Cleveland, phosphorus in, 90.
Isatin, 937.
—— action of ammonia on, 63.
—— chloride, 535.
—— brom-, chloride, 938.
—— constitution of, 937.
—— deoxyimido-, 63.
—— derivatives, 937.
—— diamido-, derivatives of, 63.
—— nitro-, 938.
—— oxyamido-hydro-, 63.
—— oxydiimido-diamido-, 63.
—— synthesis of, 534.
—— test for, 937.
—— and allied compounds, action of phosphorus pentachloride on, 535.
Isatinamide, dihydro-, 63.
Isatropic acid, 379.

Isethionic acid, preparation of, 777.
Isoamylethylsulphone, 38.
Iso-angelic acid, 706.
Isobutaldehyde, action of potassium carbonate on, 520.
Isobutane, action of bromine on, 302.
—— hexabrom-, 302.
Isobutyl alcohol, action of zinc chloride on, 1029.
—— thiacetate, boiling point of, 786.
—— di-isobutyl-glyoxylate, 47.
Isobutylformamide, 139.
Isobutylformanilide, 139.
Isobutylformic acid (inactive valeric acid) and its salts, 139.
—— —— hydroxy-, 140.
Isobutylamine, di-, 703.
—— tri-, boiling point of, 704.
Isobutylene, action of oxidising agents on, 908.
—— nitroso-di-, preparation of, 704.
Isobutyric acid and phthalic anhydride, action of sodium acetate on, 246.
Isocholesterin, specific rotatory power of, 634.
Isocymene (paramethylcumene), 624.
—— sulphonic acids, 624.
Isodiphenic acid, and its salts, 166.
—— —— constitution of, 536.
Isodipyridine and its salts, 264.
Isodulcite, 40.
—— sodium, 946.
Isoheptylic acid from β-hexyl iodide, 140.
Isohexic acid, 458.
Isoindole, 252.
—— action of hydriodic acid on, 252.
Isomalic acid, 618.
Isomerism in the propyl or tri-carbon series, 127.
Isomorphism, use of, for the determination of atomic weights, 769.
Isopentane, action of bromine on, 303.
Isophthalic acid, 536.
—— —— α-hydroxy-, 795.
—— —— β-hydroxy-, 793.
Isopropyl thiacetate, boiling point of, 786.
Isopropylacetylene, 134.
Isopropylglycocoll (amido-isobutyl-formic) acid, 140.
Isopropyls, stanno-, 918.
Isopurpurin, anthrapurpurin, and flavopurpurin, actual relations of, 943.
Isosuccinic acid, synthesis of, 783.
Isoxyhexic acid, 459.

J.

Jacobsite, 23.
Japanese wax, 1037.
Jerusalem artichoke, carbohydrates of, 778.

K.

Kellin, 1041.
Ketone from dibromethylene, 220.
Ketones, new mode of formation of, 529.
Koji, preparation of, 413.
Kino, Malabar, 159.
—— red, 159.
Kinoïn, 159.
—— constitution of, 160.
Kreunerite, 898.

L.

Lactic acid, action of phosphorus pentasulphide on, 46.
—— —— free, in milk, estimation of, 750.
—— —— monochloro-, from glyceric acid, 521.
—— —— monosulpho-, 45.
—— —— occurrence and origin of, in the animal body, 176.
Lactoglucose, 137.
Lactose, sodium, 449.
Lactuca Canadensis, milk-juice from, 1041.
Lactucarium, 1041.
Lactucerin, 1041.
Lactucic acid, 1041.
Lactucin, 1041.
Lactucone, 468.
—— hydrocarbon, $C_{14}H_{22}$, from, 469.
Lactucopicrin, 1041.
Lævulinic acid and acetopropionic acid, identity of, 453.
Lagetta furiofera, examination of, 860.
Lallementia iberica, seeds of, 822.
Lampblack, analyses of, made from the natural hydrocarbon gas of the Ohio petroleum region, 97.
Land, irrigated, agricultural experiments on, 825.
Lanthanum chlorostannate, 601.
—— distribution of, 695.
Laurent's "carminaphtha," 466.
Laurocerasus, chemical nature of the essence of, 719.
Lava from Etna, 904.
Lavez rock in the Upper Engadin, 25.
Law of molecular volumes, 197, 198.
Law of multiple proportion, proof of, 691.
—— peculiar to metallic ferrocyanides, 830.

Lead, estimation of, as lead iodate, 484.
—— estimation of traces of, 402.
—— Keith's process for desilvering and refining, by electrolysis, 288, 410.
—— presence of, in bismuth subnitrate, 80.
—— raw, Keith's process for desilvering and refining, by electrolysis, 288, 410.
—— chloride, action of salts, 1009.
—— —— action of sulphuric acid on, 1006.
—— —— electrical properties of, 427.
—— ferricyanide, 702.
—— —— with lead nitrate, 702.
—— —— with lead oxide, 703.
—— potassium ferricyanide, 702, 703.
—— sulphate, action of ammonia on, 1010.
—— —— action of certain acids on, 1006.
—— —— action of salts on, 1009.
—— —— decomposition of, by sodium chloride, 124.
—— —— estimation of, without filtering, washing, and drying, 481.
—— sulphide, action of selenium on, 771.
—— and antimony, alloys of, 889.
—— and copper, double selenides of, 440.
—— and tin alloys, behaviour of, with vinegar, 990.
Leaves, absorption of water by, 819.
Lecithin, detection of, 835.
—— digestibility of, 814.
—— in beer-yeast, 811.
Lecture experiment, use of Hempel's lamp for illustrating silver assay as a, 402.
Leidyite, 606.
Lemon, examination of distilled essence of, 386.
—— trees, stopping the gum exudation of, 821.
Leucaniline, para-, 384, 385.
Leuceïnes, 544.
Leucine obtained by the action of baryta on albumin, 544.
Leucines, 544.
Leucitophyr of Lake Averno, 609.
Leucophane, crystal form and twin formation of, 442.
Leucorosolic acid, 59.
Levulin, 778.
Levulinic acid, oxidation of, 523.
Levulose, sodium-, 449.
Life, conditions of, of the lower organisms, 664.
—— of the microzoa, relation of oxygen to, 953.
Light, action of, on silver chloride, 694.
Light, behaviour of carbohydrates towards chromates under the influence of, 911.
—— behaviour of gums towards chromates under the influence of, 911.
—— coloured, influence of, on the evaporation of water, 863.
—— influence of, on the yield of beet-sugar, 1047.
—— polarised, influence of temperature on the deviation of, by solutions of inverted sugar, 832.
—— reflected by potassium permanganate, 425.
Ligustrum ibotu, constituents of, 330.
Lime, burned, valuation of, 400.
—— solubility of, in water, in reference to the prescription for *Aqua phagedænica*, 491.
Limonin, 730.
—— and columbin, supposed identity of, 730.
Liquid bodies, expansion of, 1002.
—— heterogeneous, distillation of, 875.
Liquids, conductivity of, for heat, 1001.
—— distillation of, under the influence of static electricity, 997.
—— electromotive force produced by the flow of, through tubes, 998.
—— spectroscopic investigation of the constitution of, 101.
—— study of the molecular constitution of, by means of their coefficient of dilatation, specific heat, and atomic weight, 875.
Liquorice, glucoside of, 727.
Lithia-mica from Paris (Maine), Rozena, and Linnwald, 23.
Lithiophilite, 891.
—— analysis of, 695.
Lithium, estimation of, 830.
—— in the earths and water of the Solfatara, at Puzzuoli, 33.
—— chromate, 299.
—— dichromate, 299.
—— picrate, 789.
Litmus, substitute for, 553.
Lobster's flesh, phosphorescence of, 665.
Logwood, test for, in tea, 854.
Lotur-bark, 73.
Loturidine, 73.
Loturine, 73.
Luckite, a new variety of iron sulphate, 901.
Ludwigite, 364.
Lupigenin, 468.
Lupinin, a new glucoside, 467.
Luteo-chromium compounds, 124.
Lutidine, oxidation of, 265.
Ly-chô, a new thickening material, 187.

M.

Magnesia as an antidote for arsenious acid, 77.
Magnesium, estimation of, 969.
—— separation of, fromt he alkalis, 969.
—— volumetric estimation of, 1053.
—— carbonate, free, mixed, and combined, alkaline reaction of, 298.
—— chloride, action of, on calcium sulphide, 1012.
—— metals, volume-constitution of the sulphates, selenates, and chromates of, 768.
—— phosphide, 508.
—— silicate, alkaline reaction of, 298.
—— sulphate (epsomite), natural crystals of, of large size, 358.
Magnetic behaviour of finely-divided iron, 1000.
—— compounds of the formula $RO.Fe_2O_3$, 13.
—— oxide, new method of producing a coating of, on iron surface, 840.
Magnetite from Monte Mulatto, S. Tyrol, 23.
—— in dolerite, from Ovifak, 894.
Maize, cultivation and preservation of, 960.
—— preparation of brown-hay from, 960.
Málabar kino, 159.
Malachite-green, 84, 144, 312, 571.
—— —— remarks on Doebner's communication on, 787.
—— —— reply to the remarks of E. and O. Fischer on, 787.
Maleic acid, 372.
—— —— action of ethyl iodide on the silver salt of, 223.
—— —— bromo-, 373, 524.
Malic acid, iso-, 618.
Mallardite, a new natural manganese sulphate, 901.
Malonic acid, benzyl-, 707.
—— —— preparation of, 707, 782, 916.
Malonic acids, substituted, 707.
Malonyl urea (barbituric acid), 460.
Malt, composition of grains from, 761.
—— nutritive value of, 1050.
—— liquors, estimation of sugar in, by the ammoniacal copper test, 1066.
Malt test, 569.
Malyl, relation of oxytetric acid and its homologues to, 459.
Man during sleep, consumption of oxygen in, 75.
Manganese determination, modification of Bunsen's method, 278.
—— distribution of, in ferro-manganese alloys, 286.
—— estimation of, 277, 746.
Manganese, estimation of, especially in iron alloys, 341.
—— new method for separating ferric and aluminium oxides from, 1055.
—— separation of ferric oxide and alumina from, 970.
—— separation of, from zinc, 1055.
—— volumetric estimation of, 277.
—— alloys, 186.
—— amalgam, 693.
—— dioxide, artificial, 600.
—— peroxide battery, 1.
—— steel, 567.
—— sulphate, a new natural (mallardite), 901.
—— and aluminium, sesquisulphate of, 595.
—— and chromium, sesquisulphates of, 594.
—— and iron, sesquisulphate of, 594.
Manganosite from Langban, Sweden, 605.
Manganous chloride, action of permanganate on, 206.
—— serpentine from Langban, 32.
Mannitol, nitro-, conditions of its explosion, 777.
—— nitro-, preparation of, 777.
—— action of phosphorous pentachloride on, 917.
Mannitotetrachlor-hexine, 917.
Mannityl-hexsulphuric acid and its salts, 1034.
Mannityl-tetrasulphuric acid, 1034.
Manure, Chili saltpetre as a, for barley, 1051.
—— conversion of rags and hair into, 859.
—— effect of, on crops, 826.
—— experiments with bone-meal superphosphates, 959.
—— potassium salts as, 826.
—— artificial, 1050.
—— —— effect of, on the growth of barley and meadow land, 828.
—— —— estimation of phosphoric acid in, 1052.
—— —— experiments with, 958.
Manuring, experiments on, 1050.
—— influence of time of, in beet cultivation, 825.
Marble, imitations of, from glue, 996.
Mare's milk, composition of, 550.
Marsh-gas, detection of, in the air of mines, 673.
—— —— and hydrogen, fractional combustion of, 747.
Meadow land, effect of artificial manures on, 828.
Meal, detection of gypsum, heavy spar, &c., in, 183.
Meat, preservation of, 996.

Melissene, 782.
Mellissic acid, 782.
Melting points of organic substances, new method of determining, 673.
Melting and boiling points of solid elements, thermo-chemical relation between, 690.
Membrane, an inorganic siliceous, 199.
Mercaptan, conversion of aldehyde into, 451.
Mercurialine (methylamine), 40.
Mercuric chloriodide, 1017.
—— cyanide, decomposition of, by dilute acids alone, and in presence of sodium chloride, 1064.
—— formation of, from mercurous chloride, 889.
—— iodide, 602, 772.
—— —— melting point of, 889.
—— sulphate, action of haloïd acids on, 299.
—— sulphide, estimation of, without filtering, washing, and drying, 480.
Mercurous chloride, action of cane-sugar and lime on, 889.
—— —— formation of mercuric chloride from, 889.
Mercury, action of sulphuric acid on the haloïd salts of, 299.
—— ammoniacal compounds of, 438.
—— decomposition of haloïd salts of, 694.
—— electrolytic estimation of, 976.
—— mechanical purification of, 125.
—— presence of, in the mineral waters of Saint-Nectaire, 697.
—— production of rotatory movements in, 102.
—— purification of, 508, 602.
—— cyanide, action of bromine on, 721.
—— di-iodide, effect of heat on, 498.
—— sulphide, vapour-density of, 767.
—— and hydrochloric acid gas, reaction between, 298.
Mesitylene, 527, 623.
Mesitylenic acid, β-nitro-, and its salts, 156.
—— —— β-nitro-, melting point of, 248.
—— —— α-nitro-, and its salts, 155.
—— —— substitution-products of, 155.
Mesitylenic acids, α- and β-amido-, and their salts, 156.
—— —— α- and β-bromo-, and their salts, 156.
Mesitol, 529.
—— dibromo-, 529.
—— monobromo-, 529.
Metabenzdioxyanthraquinone, 68.
Metallic bromides, anhydrous, action of chlorine on, 770.
—— chlorides, vapour-densities of some, 1013.
—— ferrocyanides, law peculiar to, 830.
Metallic fragments, analysis of, from Peruvian tombs at Ancon (Lima), 409.
—— oxides, crystalline, formation of, by means of potassium cyanide, 1016.
—— —— preparation of finely-divided, 184.
—— phosphides, 508.
—— salts, compounds of, with compound ammonias, 376.
—— —— decomposition of, and certain inverse reactions which take place in presence of water, 1006.
—— —— galvanic properties of solutions of, 863.
—— sulphides, action of ammoniacal salts on, and its application to mineral analysis, 672.
—— —— action of organic solvents on, 771.
—— —— action of selenium on, 771.
—— —— heat of formation of, 433.
Metals, action of heat on, in a vacuum, 1018.
—— cerite, estimation of, in scheelite, 696.
—— —— examination of calcareous minerals for, 696.
—— coating with their oxides to guard them against atmospheric action, 563.
—— compounds of ethyl monochloracetoacetate with, 915.
—— decomposition of haloïd acids by, 589.
—— direct combination of cyanogen with, 909.
—— precious, state in which they exist in minerals, rocks, and artificial products, 509.
—— rare, detection of, in pyrites flue-dust, 973.
Metallurgy, copper, electrolysis used in, 760.
Metanitranisöil, behaviour of, towards ammonia, 528.
Metaxylenesulphamide, oxidation of, 53.
Metaxyloquinone, dibromo-, 530.
Meteoric iron of Hungen, 366.
—— nickeliferous iron, report on the researches of S. Meunier, relative to, 905.
Meteorite from the neighbourhood of Berdjansk, 445.
—— of the eukerite group, 610.
—— of Ysadâny, Temesvar, 609.
—— Zsadány, 210.
—— Zsadányer, analyses of, 397.
Meteorites, erosive action of strongly compressed hot gases, with reference to the history of, 1024.
—— sporadosidereal, metallic granules of, 609.

Methacrylic acid, 616.
Methaldehyde, formation of, 219.
Methane, action of bromine on, 302.
Methoxybutyramide, 523.
Methoxybutyric acid, normal, derivatives of, 523.
Methyl alcohol, action of zinc chloride on, 49, 1029.
—— —— danger of employing, in certain industries, 335.
—— —— estimation of, in wood-spirit, 487.
—— —— pure, preparation of, 520.
—— —— reaction of potassium diiodide with, 595.
—— —— and water, heat-capacity of mixtures of, 688.
—— bromobutyrate, preparation of, 523.
—— bromoterephthalate, 639.
—— butyrate, physical properties of, 521.
—— chloride, liquid, density and coefficient of expansion of, 294.
—— —— and benzene, hydrocarbons obtained by the action of aluminium chloride on, 228.
—— α-chloropropionate, physical properties of, 521.
—— crotonate, physical properties of, 521.
—— dibenzoylphenylglycerate, action of alcoholic potash on, 645.
—— formate, preparation of, 520.
—— hydrogen sulphate, 776.
—— hydroxyuvitate, 531.
—— iodide, action of water on, 700.
—— isobutylformate, 139.
—— methoxybutyrate, 523.
—— monochlorocrotonate, physical properties of, 521.
—— nitrogen chloride, 781.
—— parahydroxymesitylenate, 643.
—— paratoluate, 638.
—— propionate, physical properties of, 521.
—— sulphate, preparation of, 775.
—— thiacetate, boiling point of, 786.
Methylalizarin, 635.
Methylamine, 40.
—— action of, on acetone, 1035.
—— action of, on aurin, 926.
Methylaniline manufacture, homologous tertiary diamines obtained in, 786.
Methyl-blue, 416.
Methylbromhydroxyanthraquinone, 635.
Methylcarbopyrrolic acid, 525.
Methylcrotonic acid, 617.
—— —— hydriodo-, 618.
Methyldiacetonamine, and its salts, 1035, 1036.
Methylethylacetic acid, 618.
Methylethylsulphone, 39.
Methylhydroxyanthraquinone, 635, 636.
Methoxypropylbenzoate, 465.
Methylpropyl carbinol, prepared by synthesis, 1029.
Methylpyrrol, 525.
Methylrosaniline picrate, 84.
Methylumbelliferone, 721.
Mica, behaviour of, at high temperatures, 772.
Micas, two, intergrowth of, from Middletown, Connecticut, 363.
Microline (amazonstone) from Pike's Peak, Colorado, 515.
Microsommite, chemical composition of, 607.
Microzoa, relation of oxygen to the life of, 953.
Milarite, 358.
Milk adulteration, detection of, 1068.
—— amount of solids in, 490.
—— cow's, nucleïn from, 735.
—— estimation of free lactic acid in, 750.
—— from cows of different races, 749.
—— Marchand's method of determining butter in, 675.
—— mare's, composition of, 550.
—— new and rapid method of analysis, 80.
—— occurrence of bacteria in, 817.
—— of the cow-tree, composition of, 73.
—— testing of, for starch-powder, 674.
—— fat, quantitative estimation of, 1068.
—— sugar, reduction of cupric oxide by, 217.
Mineral analysis, use of ammoniacal salts in, 672.
—— locality, new and remarkable, with a description of several new species occurring there, 891.
—— new, occurrences in the iron-ore district of Moravicza, in the Banat, 363.
—— spring, "Marienbrunnen," near Iserlohn, Westphalia, 211.
—— —— of "Tenninger Bad," Somvixer Tobel, Grisons, 33.
—— springs of Passugg, Solis, and Tiefenkasten, 126.
—— tanning, 100.
—— water of a colliery, curious concretion balls derived from, 1024.
—— —— of Rosheim in Alsace, analysis of, 698.
—— —— Ofner Râdôczy, 211.
—— waters of Auvergne, 446.
—— —— of Buda-Pesth, 125.
—— —— of Saint-Nectaire, presence of mercury in, 697.

Mineral waters of the Couban, in the Caucasus, 125.
Minerals, application of Gaudin's atomic theory to certain, 602.
—— calcareous, examination of, for cerite metals, 696.
—— didymiferous, measurement of absorption-spectra of, 697.
—— occurring with metallic iron in the dolerite from Ovifak, 894.
—— phosphatic, composition of, 839.
Mines, detection of marsh-gas in the air of, 673.
Mio-Mio (*Baccharis cordifolia*), alkaloïd of, 1045.
Mirabilite from Aussee, 23.
Mispickel (arsenical pyrites), chemical and crystallographical examination of, 900.
Molasses, beet-root, presence of nitrils in the distillate obtained by the calcination of residues from, 612.
—— distilleries, artificial yeast for, 1078.
—— recovery of sugar from, 844.
Molecular pressure, illumination of the lines of, 573.
—— volumes, law of, 197, 198, 430.
—— weights, new, from absorption of gases by charcoal, 500.
Molecules, trajectory of, 573.
—— of liquid water, distance between the, 194.
Monimolite, 22.
Monochlorhydrin, action of ammonia on, 1031.
—— action of potassium cyanide on, 1032.
—— action of trimethylamine on, 1031.
Monochlorhydrins, 1029.
Monocyanhydrin, 1032.
Monodiferric phosphate, 202.
Monomethylglyceramine, 1031.
Mononaphthylcarbamide, 723.
Monoparamidodimethylphenyl-oxamide, 627.
Monophenylarsinic acid, action of, on animals, 476.
Monophenyltriethyl-arsenium iodide, 162.
Monosulpholactic acid, 45.
Mordant for Turkey-red dyeing, 187.
Morphine, absorption-spectra of, in solution, 269.
—— action of iodic acid, sulphomolybdic acid, and ferric chloride on, 70.
—— colour reaction with antimony trichloride, 831.
Mosandrite, crystal system of, 608.
Mosandrium, the supposed new element, 12, 117.
Mother of pearl, artificial, manufacture of, 996.
"Moto," preparation of, 414.
Mucic acid, dehydro-, 783.
—— —— dehydro-, action of sodium-amalgam on, 783.
—— —— dehydro-, two new acids from 783.
—— —— derivatives of, 783.
Mucilage of beet, 660.
Mucobromic acid, and its salts, 224.
—— —— bromo-, 224.
—— —— relation of dibromopyromucic acid to, 918.
Mucobromic aldehyde, 918.
Muconic acid, chloro-, 917.
Mulberry tree, disease of, 821.
Multiple proportion, proof of the law of, 691.
Murexide, synthesis of, 375.
Must, aëration of, 492.
—— fermentation of, 993.

N.

Nagyagite, 898.
Naphthalene, action of phthalic anhydride on, 940.
—— azodibromosulphoxylbenzene, dioxy-, 317.
—— bromo-, nitration of, 721.
—— bromo-, oxidation of, 807.
—— colour reaction with antimony trichloride, 831.
—— colour-reaction of, with bismuth trichloride, 831.
—— dinitrobromo-, 722.
—— nitro-, nitrophthalic acid from, 644.
—— nitro-, oxidation of, 722.
—— trichloro-, new, 722.
—— ζ-trichloro-, 723.
—— trinitrobromo-, 722.
α- and β-naphthalenediamine, 232.
Naphthalene-β-sulphonic acid, dichloro-, and its salts, 722, 723.
Naphthalene-β-sulphonic chloride, action of chlorine on, 722.
—— —— dichloro-, 723.
—— —— tetrachloride of, 723.
—— —— tetrachloride of, constitution of, 723.
Naphthalide, bromaceto-, 165.
—— dibromaceto-, 165.
β-Naphthimido-acetate, 48.
β-Naphthimidoamide hydrochloride, 48.
β-Naphthimido-ethyl-ether hydrochloride, 48.
β-Naphthimido-isobutyl-ether, 48.
β-Naphthimido-isobutyl-ether hydrochloride, 48.

Naphthol, amidodiimido-, 251.
—— amidodiimido- chromate, 251.
—— amidodiimido- hydrochloride, 251.
—— azobenzene-β-sulphoxyl-, 316.
—— triamido- stannosochloride, 251.
—— triamido- sulphate, 251.
—— trinitro-, 250, 722.
—— trinitro-, constitutional formula of, 251.
α- and β-naphthol, metazosulphoxylbenzene-, 316.
β-Naphthol, azonaphthalenesulphoxyl-, 316.
—— halogen-derivatives of, 722.
—— monobromo-, 722.
β-Naphtholsulphonic acid, parazosulphoxylbenzene-, 316.
Naphthonitril, chlorination of, 721.
Naphthopicric acid, and some of its derivatives, 250.
Naphthylamine ethyl-, 147.
Naphthylarsinic acid, 68.
Naphthylcarbamides, 723.
Naphthyl-phosphorous acid, 67.
Narceine, colour reaction with antimony trichloride, 832.
Narcotine, colour reaction with antimony trichloride, 831.
Naringin, 468.
Nascent state, 864.
Nepheline, chemical composition of, 606.
—— rock of Meiches in the Odenwald, 607.
Nettle, analysis of, 821.
Nickel, complex oxides of, 507.
—— detection of, 179.
—— estimation of, by precipitation as oxalate, 1054.
—— malleable, preparation of, and its application in the pure state, 563.
—— metallurgy of, 285.
—— separation of ferric oxide and alumina from, 970.
—— separation of zinc from, 276.
—— amalgam, 693.
—— hydrate, estimation of, without filtering, washing, and drying, 481.
—— oxide, Ni_3O_4, 299.
—— and cobalt sulphates, chemical equivalence of, 876.
Nicotine, 731.
—— action of hydriodic acid on, 731.
—— action of hydrochloric acid on, 731.
—— action of sulphur on, 732.
—— derivative, a new, 732.
—— oxidation of, 732.
—— oxidation products of, 808.
—— preparation of, 808.
—— reaction with antimony trichloride, 831.
—— and zinc, double chloride of, distillation of, with soda-lime, 809.
Nicotinic acid, 808.
—— —— action of phosphorus pentachloride on, 809.
Nile, waters of, amount of nitric acid in, 905.
Niobates, analysis of, 12.
Nitracetoparaxylide, 52.
Nitrates, estimation of, in very dilute solutions, 1062.
—— in sugar-beets, 826.
Nitre, loss of, in the vitriol manufacture, 838.
Nitric acid, amount of, in the waters of the Nile, 905.
—— —— estimation of, 79.
—— —— estimation of, as ammonia, 79.
—— —— estimation of, by potassium dichromate, 399.
—— —— estimation of, in well water, 274.
—— —— quantitative spectroscopical estimation of, 829.
Nitric oxide, action of, on blood, 817.
—— —— action of potassium pyrogallol on, 1012.
—— —— density and decomposition of, 195.
Nitrification, 1046.
Nitrils, conversion of, into imides, 46.
—— presence of, in the distillate obtained by the calcination of residues from beet-root molasses, 612.
Nitrites, formation of, in the soil, 737.
Nitro-alizarin (alizarin-orange), 84.
Nitrogen, atmospheric, absorption of, by plants, 818.
—— estimation of, 961.
—— estimation of, in organic bodies, 80.
—— estimation of, in the analysis of agricultural products, 962.
—— estimation of, in urine, 829.
—— modification of Simpson's method for estimating, 554.
—— presence of, in steel, 1017.
—— quantity of, which must be supplied to plants to ensure their normal development as field crops, 668.
—— supply of, to plants, 739.
—— acids, behaviour of, with sulphuric acid, 770.
—— chlorides, substituted, 780.
—— iodide, 882.
—— tetroxide, absorption spectra of 191.
—— —— action of sulphuric acid on, 770.
—— carbon, and hydrogen, simultaneous determination of, 278.
Nitroglycerol, 1032.
Nitromannite, conditions of its explosion, 777.

Nitromannite, explosion of, 1080.
—— preparation of, 777.
Nitrometer, 79.
Nitrophthalic aldehyde, 722.
Nitrosothiohydantoïn, and its salts, 712.
Nitrosyl-silver, action of, on organic bodies, 309.
Nitrosylsulphuric acid, behaviour of, with sulphuric acid, 771.
—— —— preparation of, 383.
Nitrotoluene, commercial, presence of metanitrotoluene in, 625.
Nitrous acid, detection and estimation of, in potable waters, acids, &c., 964.
—— —— estimation of, 79.
—— —— oxidation of, by ozone and by moist oxygen, 9.
—— —— preparation of, 200.
Nitrous anhydride, existence of, in the gaseous state, 502.
Nontronite, 31.
North Sea, results of the Norwegian expedition to, 1060.
Norwegium, a new metal, 890.
Norwegian expedition to the North Sea, results of, 1060.
Nucleïn, digestibility of, 814.
—— from cow's milk, 735.
—— in beer-yeast, 811.
Numeite, a new jewel, 184.

O.

Oenanthylic acid and its salts, 1037.
Oil of wine, 615.
—— Turkey-red, analysis of, 984.
Oils, determination of free acids in, 406.
—— testing lubricating-, 292.
Oil-seeds, advantages of only partially removing the fat in, 99.
Olefines, action of oxidising agents on, 907.
—— reactions of the halogen-compounds of, 34.
Olives, proper time for pressing, 1080.
Orange, analysis of, 1049.
α-Orcendialdehyde, 720.
β-Orcendialdehyde, 720.
α-Orcendialdehydedianilide, 720.
Orcin. See Orcinol.
Orcinol, aldehydes from, 719.
—— parazosulphoxylbenzene, 316.
—— trinitro-, preparation of, 717.
Orcylaldehyde, 720.
Orcylaldehyde anilide, 720.
Ores, fahl-, extraction of silver from, 755.
Ores, method of removing phosphoric acid from, 91.
—— treatment of, containing silver and copper, 496.
Organic acid, a new, from bromocitraconic acid, 1037.
Organic acids, action of phosphorus pentasulphide on, 45.
—— —— monobasic, amidines and thiamides of, 922.
Organic base, a new, in the animal organism, 72.
—— bases, compounds of, with mercuric chloride, 231.
—— compounds, action of nitrosyl-silver on, 309.
—— —— containing halogens or nitrogen, analysis of, 555.
—— —— high-boiling, vapour-densities of certain, 1025.
—— —— solid, specific gravity determinations of, 610.
Organic matter, estimation of, in natural waters, 976.
Organism, animal, behaviour of phenol in, 816.
—— —— oxidations in, 814.
—— —— syntheses in, 814.
—— —— behaviour of ammonium chloride in, 830.
—— of warm-blooded animals, influence of the temperature of the surrounding air on the processes of decomposition in, 75.
Organs of animals, healthy, existence of bacteria or their germs in, 1045.
Orthocresol, 323.
Orthocresolphthaleïn, 634.
—— bromine derivatives of, 635.
—— diacetyl and dibenzoyl derivatives of, 635.
Orthocresolphthalideïn, 636.
Orthocresolphthalidin, 635.
Orthocresolphthalin, 635.
Orthoformylglucoside, or helicin, synthesis of, 1038.
Orthonaphthoylbenzoic acid, 940.
Orthophthalic acid, hydroxy-, 795.
—— —— methoxy-, 793.
Orthose, artificial crystallisation of, 359.
Orthosulphobenzoic acid, 629.
Orthotoluenesulphonamide, oxidation of, 628.
Orthotolylenediamine derivatives, 715.
Orthoxylene, 655.
—— separation of, from its isomerides, 919.
Oxalic acid, action of potassium permanganate on, 205, 353.
—— —— not poisonous (?), 335.

Oxamide, diethyl-, action of phosphorus pentachloride on, 784.
—— di-isobutyl-, from commercial trimethylamine, 912.
—— dipropyl-, from commercial trimethylamine, 912.
—— thiodiethyl-, 784.
Oxidation, rapid, new application of, by which sulphides are utilised for fuel, 755.
Oxides, crystalline metallic, formation of, by means of potassium cyanide, 1016.
Ox-imido-ether, 47.
Ox-imido-ether, hydrochloride of, 47.
Oxindole, aceto-, 937.
—— aceto-, action of soda on, 937.
—— nitro-, 938.
Oxyadipic acid, preparation of, 706.
α-Oxyanthraflavone, 383.
β-Oxyanthraflavone, 384.
Oxyanthraxanthin, 384.
Oxyanthraquinone, monacetyl-, 654.
Oxyanthraquinones, tri-, 942.
Oxyanthrarufin, 259.
—— constitution of, 942.
Oxybenzyl alcohols, homo-, xylenols, hydroxytoluic aldehydes and acids, alcohol- and aldehyde-hydroxybenzoic acids, and hydroxyphthalic acids, relation between, 924.
Oxychinolinecarboxylic acid, 472.
Oxychrysazin, 942.
Oxycinchonic acid, 472.
Oxygen, estimation of, in blood, 835.
—— evolution of, by plants in sunlight, 819.
—— photographed spectrum of, 497.
—— polarisation, changes in the surface of platinum and palladium produced by, 1005.
—— presence of dark lines in the solar spectrum, which correspond closely with the lines of the spectrum of, 997.
—— relation of, to the life of the microzoa, 953.
—— relative affinity of, for carbonic oxide and hydrogen, 436.
—— Schützenberger's process for the volumetric estimation of, in water, 77.
—— spectrum, 497, 861.
—— tension of, in arterial blood, 811.
—— and the halogens, reciprocal displacements of, 351.
—— and the halogens, relative affinities of, 351.
—— sulphur, and the halogens, reciprocal displacements between, when combined with hydrogen, 296.
Oxyheptic acid, homologues of, 458.
Oxyhexic acid, 459.
Oxyketones, synthesis of, 319, 638.
—— synthesis of, by introducing acid radicles into phenols, 319.
Oxymalonyl-urea (dialuric acid), 460.
Oxymesitylenic acid, constitution of, 247.
α-Oxynaphthoic acid, action of diazosulphobenzoic acid on, 317.
Oxypentic acid, 458.
Oxyphenylacetic acid, 322.
—— —— dinitro-, 322.
—— —— nitro-, 322.
Oxyphenylthiocarbimide, 314.
Oxypyromecazonic acid and its salts, 710
Oxypyrometazonic acid, 708.
Oxytetric acid, 458.
—— —— and its homologues, relation of, to malyl and other radicles of the bibasic acids, 459.
Ozokerite, 896.
—— composition of a nodule of, found at Kinghornness, 1020.
Ozone, 8, 435.
—— from permanganate and oxalic acid, 353.
—— formation of, by hydrocarbons, 592.

P.

Pæonia Moutan, 306.
Pæonia peregrina, chemistry of, 1043.
Palladium, atomic heat of hydrogen in its combination with, 590.
—— changes in the surface of, produced by oxygen-polarisation, 1005.
—— specific heat and latent heat of fusion of, 294.
Palmella cruenta, colouring matter of, 1042.
Palmellin, 1042.
—— decomposition of, 1042.
Pancreatic digestion, 814.
Papaverine, new test for, 1067.
—— reaction with antimony trichloride, 832.
Paper for pigment or carbon photography, 560.
—— quantitative estimation of starch in, 180.
—— resin-sizing of, 994.
Pavy's process for estimation of sugar, 557, 834.
Parabanic acid, constitution of, 620.
—— —— ditolyl-, 54.
—— —— —— oxidation of, 62.
Parachlorobenzyl chloride and bromide, 62.
Paracresol, 789.

Paracresol, action of bromine on, 789.
—— tetrabromo-, 789.
Paradiphenylbenzene, 466.
Paraffins, boiling points of, 765.
—— nitration of derivatives of, 700.
Paraglobulin, 472.
Parahydroxysalicylic acid, 928.
Paramethylcumene (isocymene), 624.
Para nuts, substance from, 950.
Paraphenylenediamine. See Phenylenediamine.
Parapropylbenzenesulphonic acid, 631, 632.
Parapropylphenol, 632.
Pararosaniline, 385.
—— trimethyl-, 926.
Parathionic acid, 777.
Paratoluamide, 638.
Paratoluanilide, 638.
Paratoluene sulphydrate, action of sulphuric monochloride on, 230.
Paratoluic acid, 638.
Paratoluidine cobalt chloride, 461.
Paratolyldiphenylmethane, 385.
Paratolylenediamine and its salts, 715.
Paricine, 1043.
Pear wine, 1078.
Péchiney's black ash process, 752.
Pelagosite, 604.
Pelletierine from pomegranate bark, 170.
Pennsylvanian petroleum, crystalline products from, 309.
Pentamethylbenzene, 527.
Pentamethylethol, 46.
Pentathionic acid, 1012, 1013.
Pentic acid, 457.
Pentlandite or pyrrhotine in dolerite from Ovifak, 894.
Peonin, 926.
Peptone, chemical nature of, 660.
—— fibrin-, action of acetic anhydride on, 950.
—— regeneration of albumin from, 950.
Peptones, chemical composition of, 811.
Perbromination, 702.
Perchlorination, 721.
Petrocene, 1026.
Petroleum, American, hydrocarbons from, 447.
—— —— unsaturated hydrocarbons resulting from the decomposition of, 1025.
—— —— and Russian, investigation of, 1076.
—— Pennsylvanian, crystalline products from, 309.
—— spirit and benzene, characteristic differences between, 1063.
Phenanthraquinone, action of ammonia on, 718.
Phenanthrene, colour reaction with antimony trichloride, 831.
—— colour reaction with bismuth trichloride, 831.
—— constitution of, 538, 653.
—— nitro-, and its derivatives, 941.
—— perchlorination of, 721.
Phenanthrenequinone, 538.
—— preparation of, 165.
—— and its imide, constitution of, 539.
Phenanthrenequinonimide, 539.
Phenetol, α-dinitro-, 717.
—— metanitro-, 238.
Phenol, action of fused soda on, 633.
—— action of nitric acid on, 148.
—— behaviour of, in the animal organism, 816.
—— derivatives, heat of formation of, 874.
—— distinctive tests for, 182.
—— formation of aurin from, 789.
—— formation of, from putrefying albuminoïd matter, 1037.
—— azobenzenesulphoxyl-, 315.
—— dibenzoyl-dinitro-, 148.
—— dibromonitro-, 148.
—— α-dinitro-, preparation of ethers of, from α-dinitro-chlorobenzene, 716.
—— dinitro-amido-, action of soda-solution on, 717.
—— β-dinitroparabromo-, and its compounds, 50.
—— metadinitro-, sulphide of, 714.
—— metanitro-, and its derivatives, 237.
—— metazosulphoxylbenzene-, 315.
—— orthamido-, new colouring matter from, 924.
—— orthonitro-, derivatives of, 314.
—— parazosulphoxylbenzene-, 315.
—— —— orthonitro-, 316.
—— perchloro-, chloride of, 463.
—— tribromo-, 55, 789.
—— —— bromide of, 717.
—— trinitro-, ethers of, 923.
Phenoldidiazobenzene, 148.
α-Phenoldisulphonic acid, derivatives of, 933.
Phenolglucoside, synthesis of, 1038.
Phenolglycollic acids, 929.
Phenolphthaleïn, constitution of, 637.
—— conversion of diphenylphthalide into, 637.
—— use of, in titration, 273.
Phenols, action of some diazosulphonic acids on, 315.
—— etherification of, 215.
—— dinitro-, 238, 928.
—— nitro-, action of nitric acid on, 148.
—— —— three isomeric, heat evolved by the action of sodic oxide on, 768.

Phenoxypropionic acid, 642.
—— —— monobromo-, 642.
Phenyl-hydrogen sulphate and similar derivatives of the phenols, 148.
—— potassium sulphate, 148.
Phenylacetic and phenylpropionic acids, physiological relations of, 662.
Phenylacetimidothioethyl ether, 922.
Phenylacetone, 795.
Phenylallyl ether, *a*-dinitro-, 717.
Phenylamidacetic acid, 322.
—— —— action of phosphorus pentachloride on, 322.
Phenylamidopropionic acid (amidohydrocinnamic acid), 378.
Phenyl-anisaldehydine, 234.
Phenylarsenic acid, 161.
Phenylarsenious chloride, 161.
Phenyl-benzaldehydine and its salts, 234.
Phenylbenzoic acid and its salts, 164.
—— —— nitro-, 164.
Phenylchloride, isocyano-, 805.
Phenylcinnamic acid, 640.
Phenylcyanamide, preparation of, from monophenylthiocarbamide, 804.
Phenyldiphosphorosulphocarbonic acid, 528.
Phenyl-duryl-carbonyl, 713.
Phenylene-carbamide, 314.
Phenylenediamine, para-, 462.
—— —— chloro-, formation of, 144.
—— —— para-, hydrochloride, action of bleaching-powder on, 462.
—— —— methyl-derivatives of, 626.
—— —— nitrochloro-, 310.
Phenylethylamine hydrochloride, decomposition of, 922.
Phenylethyl-sulphide, 37.
Phenylethylsulphone, 39.
Phenylfurfuraldehydine and its salts, 235.
Phenylglyceric or styceric acid, 644, 645.
Phenylglycol, hydrocarbon, $C_{16}H_{12}$, from, 327.
Phenylglyoxylic acid, 648.
—— —— amides of, 649.
—— —— new method of preparing, 322.
Phenylmercaptan, bromo-, 803.
Phenylmercapturic acid, bromo-, 803.
—— —— bromo-, action of alkalis on, 803.
—— —— bromo-, action of hydrochloric or dilute sulphuric acid on, 803.
Phenylnaphthalene, colour reaction with antimony trichloride, 831.
Phenyl *a*-dinitro-phenate, 717.
Phenylphosphine, reactions of, 528.
Phenylpropionic and phenylacetic acids, physiological relations of, 662.
Phenyl sulphide, chloronitro-, 231.
—— —— metadinitro-, 230.
Phenylthiocarbamic acid, 54.
Phenylthiocarbimide, action of sulphuric anhydride on, 312.
Philippium, 116, 204.
Phillipsite from Sirgwitz, twin-formation of, 515.
Phlobaphenes, 979.
Phloroglucinol, 934.
—— oxidation of resorcinol to, 633.
—— synthesis of, 633.
—— Weselsky's reaction for, 979.
—— trinitro-, and its salts, 57.
—— trinitroso-, 57.
—— tannins, detection of, 979.
Phorone, isomeride of, 726.
Phosgenite from Monte Poni, Sardinia, 604.
Phosphates, process for enriching, 490.
—— studies of the, 201.
Phosphatic minerals, composition of, 839.
Phosphenyl chloride, homologue of, 721.
Phosphides, metallic, 508.
Phosphoric acid, estimation of, 966.
—— —— estimation of, as ammonium phosphomolybdate, 275.
—— —— estimation of, as phosphomolybdate, 482.
—— —— estimation of, in artificial manures, 1052.
—— —— estimation of, in fish guano, 968.
—— —— insoluble, in superphosphate, 1052.
—— —— method of removing, from ores, 91.
—— —— quantitative spectroscopical estimation of, 829.
—— —— ratio of, to sugar, in the root and leaves of the beet, 818.
—— —— separation of, from its salts, 972.
—— —— soluble, estimation of, in superphosphates, 672, 745.
Phosphorus in ancient iron, 1074.
—— in carbon bisulphide, explosive product of a solution of, 996.
—— in Cleveland ironstone and in iron, 90.
—— separation of, in open hearth, puddling furnace, and Bessemer converter, 185.
—— solubility of, 104.
—— bisulphide, 691.
—— pentasulphide, 691.
—— —— vapour-density of, 579.
—— sulphides, 883.
Phthalanils, substituted, 323.
Phthaleïn, action of nitric acid on, 635.
Phthalic acid, nitro-, 722.

Phthalic acid, nitro-, action of hydriodic acid on, 644, 722.
—— —— nitro-, action of hydrobromic acid on, 644, 722.
—— —— nitro-, obtained by oxidation of nitronaphthalene, 644.
—— —— nitrodichloro-, 723.
—— acids, methoxy-iso-, 793.
—— aldehyde, nitro-, 722.
—— anhydride, action of, on naphthalene, 940.
—— —— vapour-density of, 1025.
—— —— and isobutyric acid, action of sodium acetate on, 246.
Phthalimide, metanitrophenyl-, 324.
—— parabromophenyl-, 324.
—— parachlorophenyl-, 323.
—— paraiodophenyl-, 324.
Phthalimidobenzoic acids, ortho- and meta-, 324.
Phthalophenone (diphenylphthalide), conversion of, into phenolphthaleïn, 637.
—— constitution of, 636.
Phthalyl alcohol, 634.
Phthalylpropionic acid, derivatives of, 245.
Photographed spectra of oxygen and hydrogen, 497.
Photographic negatives, intensifying, by means of potassium sulphide, 184.
Photographing bacteria, 1046.
Photography, pigment or carbon, preparation of paper for, 560.
Photo-lithography, 836.
Phyllite, or sericite-gneiss, 207.
Phylloxera, saccharine matter contained in vines suffering from, 1049.
Physiological relations of phenylacetic and phenylpropionic acid, 662.
Phytolacca decandra, colouring matter of, 730.
Picoline, action of chlorine on, 264.
—— oxidation of, 265.
—— and its derivatives, 262.
—— platino-chloride, decomposition-products of, 264.
Picramic acid, action of soda-solution on, 717.
Picramide and aniline, 51.
Picrosclerotine, 270.
Picrotephroite from Laangban, 32.
Picrotoxide, benzoyl-, 729.
—— hydrate of, preparation of, 729.
Picrotoxin, 729.
—— action of acetic anhydride and sodium acetate on, 729.
—— action of bromine on, 729.
—— and some of its derivatives, characteristic reactions of, 748.
Pig-iron, dephosphorisation of, 1075.
—— —— estimation of silicon in, 974.
Pig-iron, highly siliceous, preparation and use of, 678.
—— —— manganiferous, preparation of, 755.
—— —— white, specific gravity of, 840.
Pigment, green, from barium chromate, 987.
Pig-metal, effect of phosphorus on, 92.
—— —— methods of removing phosphorus from, 92.
Pinacolins, 317.
Pinacone, chemical structure of, 536.
Pinacones, 317.
Pinguite, 31.
Pink, garden, ash of the, 338.
Piperidine, 733.
—— hydrochloride, action of bromine on, 733.
Pipturus argenteus, examination of, 860.
Pittacal, 253.
Plagioclase basalts, 903.
—— granular, in the limestone strata of Geppersdorf, 903.
Plant respiration, 736.
Plantain, analysis of, 821.
Plants, absorption of atmospheric nitrogen by, 818.
—— absorption of selenium by, 955.
—— assimilation of soda by, 666.
—— cultivated, diseases of, 820.
—— in sunlight, evolution of oxygen by, 819.
—— influence of atmospheric electricity on, 818.
—— quantity of nitrogen which must be supplied in order to ensure their normal development as field crops, 668.
—— sarcophytic and parasitic, replacing the carbonic acid of the air necessary for the production of chlorophyll in, by organic substances, 737.
—— supply of nitrogen to, 739.
—— supposed existence of hydrogen peroxide in the organism of, 665.
Platinum, changes in the surface of, produced by oxygen polarisation, 1005.
—— incandescent, radiation from, 573.
—— polarisation of, 578.
—— pure, preparation of, 772.
—— alloy assay, 555.
—— water-cell, quantity of electricity necessary for charging a, 194.
Plinian, so-called, 901.
Poisoning fowls with pumpkin seeds, 1046.
Poisons, metallic, Verrykin's method of detecting, 973.

Polarisation, galvanic, 577.
—— voltaic, capacity of, 864.
Polydymite, 18.
Polygonum tinctorium, preparation of indigo-blue from, 532.
Polyporic acid, 382.
—— —— chlorinated compounds of, 383.
—— —— hydro-, and its salts, 383.
—— —— nitro-, 383.
Pomegranate, alkaloïds of, 657.
—— bark of the root of the, 169.
Pompeii, a thread-like substance found in the excavations of, 680.
Poppy petals, composition of the ash of, 395.
Porcelain earth of Limoges, 87.
Porter, Dublin, and Burton ales, analysis of, 344.
Portland cement, hardening theory of, 408.
Portulacca, analysis of, 821.
—— colouring-matter of, 730.
Position, experimental determinations of, 232.
Potable water, preservation of, 85.
Potash, improvements in the manufacture of, 422.
—— mica, crystal-system of, 24.
Potassium amalgam, action of dilute hydrochloric acid on, 864.
—— —— action of water on, 864.
—— bromide, action of oxygen on, 770.
—— chloride, heat absorption on solution in water, 588.
—— cobaltocyanide, 303.
—— ferrocyanide, action of ammoniacal copper sulphate on, 775.
—— —— action of bromine on, 702.
—— —— a process for utilising the residue from the manufacture of, 680.
—— fluoride, compound of chromic acid with, 1016.
—— hydrate, action of the vapour of, on red hot iron, 887.
—— hydrocoerulignone, 253.
—— hydrosulphide, heat of formation of, 865.
—— —— heat of hydration of, 866.
—— iodide, iodated, 595.
—— —— lead in commercial, 504.
—— —— manufacture of, 504.
—— —— reaction of with sulphurous acid, 352.
—— malonate, electrolysis of, 917.
—— mesitylenesulphonate, products of the action of fused potash on, 529.
—— nitrite, preparation of, 595.
—— nitrate, estimation of minute quantities of soda in, 399.
—— permanganate absorption spectra of, 189.
Potassium permanganate, action of manganous chloride on, 206.
—— —— alkaline, some reactions of, in the moist combustion process, 555.
—— —— and oxidation products obtained by its use, 204.
—— —— the light reflected by, 425.
—— salts as a manure, 826.
—— —— behaviour of, in the blood, 816.
—— sulphides, heat of formation of, 865.
—— sulphocyanide, action of potassium permanganate on, 205.
—— thiocyanate, behaviour of, with some of the cinchona alkaloids, 281.
—— ultramarine, 692.
—— xanthorhamnin, 272.
Potato, composition of the growing, 174.
—— cultivation, 823.
—— fusel-oil, alcohols in, 36.
—— spirit, preparation of pressed yeast as a bye-product from, 843.
Potstone of Chiavenna, 26.
Powdered substances, determination of the specific gravity of, 669.
Precipitates, estimation of, without filtering, washing, and drying them, 480.
Pressure, influence of, on the spectra of vapours and gases, 685.
Pressures produced by galvanic deposits, 576.
Printing, heliographic, 750.
—— —— on sheet-zinc, 751.
Propane, action of bromine on, 302.
Propanes, chlorobromo-, 131.
—— dibromo-, 129.
—— —— two isomeric, 908.
—— dichloro-, 128.
Propenyl-benzoic acid, 157.
—— —— hydroxy-, 465.
Propionamide, 47.
Propionamidine, or propionimidamide, hydrochloride of, 47.
Propionic acid, dichloro-, from glyceric acid, 521.
Propionimidamide or propionamidine, hydrochloride of, 47.
Propionitril, action of hydrochloric acid and alcohol on, 47.
Propyl or tri-carbon series, isomerism in, 127.
—— alcohol, normal, action of zinc chloride on, 1029.
—— glycol, symmetrical, 132.
—— —— symmetrical, chlorhydrins of, 133.
—— thiacetate, boiling point of, 786.
—— —— iso-, boiling point of, 786.
Propylbenzene, 631.
Propylbenzoic acid, 142, 321.

Propylbenzoic acid, hydroxy-, 139, 157, 465.
—— —— hydroxy-, derivatives of, 795.
—— —— hydroxy-, oxidation-products of, 795.
Propylene, action of oxidising agents on, 907.
—— bromide, action of water on, 700.
—— —— conditions under which it is formed, 908.
—— glycol, dehydration of, 136.
—— oxide, symmetrical, 133.
Propylenes, bromo-, 130.
—— chloro-, 128.
—— polyoxy-, 133.
Propylhydroxybenzoic acid (cumenol-carboxylic acid), 642.
α-Propylphenol, and its derivatives, 631.
β-Propylphenol, 632.
Propylphenolcarbonic acid, ortho- and para-, 632, 633.
Propyls, stanno-, 918.
Protagon, 950.
Protocatechuic acid, 933.
—— —— action of nitrous anhydride on, 643.
Pseudobrookite, a new mineral, 441.
Pseudocumene, 527, 623.
Pseudopurpurin, absorption-spectrum of, 807.
Pseudorosolic acid, 58.
Pseudouric acid, 784.
Ptomaines, 734.
Ptyalose, so-called, 370.
Pumpkins, analyses of, 961.
Pumpkin-seeds, fowls poisoned with, 1046.
Purpurin, 256.
—— absorption-spectrum of, 807.
Purpurins, isomeric, chronology of, 943.
Putrefaction, formation of cresols during, 789.
—— of albumin, aromatic products of, 806.
Pyrene, colour reaction with antimony trichloride, 831.
Pyrethrum, flowers of, active principle of, 808.
Pyridine, 733.
—— dibromo-, 733.
—— monobromo-, 734.
Pyridenedicarbonic acid, and its salts, 731.
—— —— identity of, with cinchomeronic acid, 947.
Pyridene-tricarbonic acid, 657.
Pyrites, auriferous, examination of, 509.
—— extraction of gold, silver, and other metals from, 288.
—— flue-dust, detection of some rare metals in, 973.
Pyrocholesteric acid, 388.
Pyrocinchonic acid, 947.
Pyromecazonic acid, and its salts, 708, 710.
—— —— oxy-, and its salts, 710.
Pyromeconic acid, 307.
—— —— and its salts, 708.
—— —— amido-, 709.
—— —— hydronitroso-, 307.
—— —— nitro-, 307.
—— —— nitro-, and its salts, 709.
—— —— nitroso-di-, 708, 709.
Pyrometazonic acid, oxy-, 708.
Pyromucic acid, dibromo-, relation of, to mucobromic acid, 918.
Pyromucic acids, monobromo-, 308.
Pyrophoric iron, 119.
Pyropissite, composition of, 1021.
Pyroracemic acid, 524.
—— —— action of phosphorus pentasulphide on, 46.
—— —— synthesis of, 45.
Pyrotartaric acid, action of phosphorus pentasulphide on, 45.
—— —— symmetrical, 133.
—— chloride, 134.
Pyroxene (augite), varieties of, 364.
Pyroxylin, conversion of hydrocellulose into, 911.
Pyroxylins, 372.
Pyrrhotine or pentlandite, in dolerite, from Ovifak, 894.
Pyrrol, 524.
—— derivatives, 525.
—— synthetic preparation of, 526.
Pyruvic acid, formation of, from tartaric acid, 916.

Q.

Quantitative analytical method, a new, 969.
Quartz, behaviour of, with microcosmic salt, 79.
—— crystals, etch-figures on, 439.
—— —— from Krummendorf, growth-phenomena of, 901.
Quartz-diorite from Yosemite, 512.
Quebracho wood, 996.
Quercetin, acetyl-, 945.
—— dibromo-, 945.
—— dibromacetyl-, 945.
—— formulæ of, 944.
—— sodium-, 945.
—— tetrabromo-, 946.
—— tetrabromodiacetyl-, 946.
Quercetin, formulæ of, 944.
—— potassium-, 946.
—— tetrabromo-, 945.
Quercitan, 241.
—— monaceto-, 241.

Quercitan, monochlorhydro-, 241.
Quercite, action of hydrobromic and hydriodic acids on, 241.
—— action of phosphorus pentachloride on, 917.
—— monobromhydro-, 241.
—— preparation and properties of, 239.
Quercites, aceto-, 240.
—— butyro-, 241.
—— chlorhydro-, 241.
Quinamine and its salts, 1044.
Quinic acid, 159.
—— —— preparation of, from hay, 952.
Quinidine, test for, 281.
—— sulphate, 656.
Quinine alkaloïds, iodosulphates of, 982.
—— citrates, 1043.
—— determination of, in certain of its salts, 488.
—— α-dihydroxyl-, 809.
—— estimation of in *Ferri et Quinæ citras*, B.P., 405.
—— formation of cinchomeronic acid from, 947.
—— hydrochloride, test for, 281.
—— isobutylformate, 139.
—— oxidation of, 946.
—— oxidation of, by potassium permanganate, 541.
—— oxidation-products of, 809.
—— reaction with antimony trichloride, 832.
—— salt, a new, 169.
—— substitutes for, 71.
—— test for, 280.
—— test for the purity of, 982.
Quininic acid, 810.
Quininum dimuriaticum carbamidatum, 169.
Quinol (hydroquinone), 462.
—— derivatives of, 464.
—— diacetyl-, 718.
—— dinitro-diethoxy-, 464.
—— mononitro-diethoxy-, 464.
Quinoline from cinchonine, oxidation of, by potassium permanganate, 731.
—— oxidation of, 731.
Quinone, action of acetic anhydride and sodium acetate on, 718.
—— dichlorodibromo-, 462.
—— tetrabromo-, 718.
Quinones, action of ammonia on, 718.
Quinonimide, chloro-, 924.

R.

Racemic acid, 223.
Rags, conversion of, into manure, 859.
Rain, action of, on clover hay, 823.
Red pigment, manufacture of a, from iron scrap, 97.
—— ultramarine, 885.
—— wine, making, 681.
—— —— pressing of, 681.
Reddingite, 892.
Residues obtained in the manufacture of aniline-red, utilisation of, 995.
Resin-sizing of paper, 994.
Resoquinhydrone, tetrabromo-, 465.
Resorcin. See Resorcinol.
Resorcin-blue, 292.
Resorcinol, 238, 927.
—— azosulphoxylene-, 316.
—— benzo-, 319, 320.
—— bromide, tribromo-, 717.
—— dibenzo-, 319, 320.
—— ethers, action of nitrous acid on, 465.
—— ethoxydinitro-, 465.
—— ethoxymononitroso-, 465.
—— manufacture of, 291.
—— metazosulphoxylbenzene-, 316.
—— oxidation of, to phloroglucinol, 633.
—— parazosulphoxylbenzene-, 316.
—— pentabromo-, 464.
—— —— action of aniline on, 55.
—— —— action of tin and hydrochloric acid on, 55.
—— tetrabromodi-, 55.
—— tribromo-, 55, 464.
—— trinitro-, 238.
—— trinitro-, preparation of, 717.
—— vapour-density of, 1025.
Resorcinol-disulphonic acid and its salts, 934.
—— —— —— fusion of, with potash, 934.
Respiration, plant, 736.
Respiratory movements, influence of, on the formation of carbonic acid, 75.
Retinalites, 301.
Retinindole, 535, 938.
Retinite, Russian, 441.
Rhamnetin, formula of, 271.
—— acetyl-, 271.
—— benzoyl-, 272.
—— dibromacetyl-, 272.
—— dibromo-, 272.
—— dimethyl-, 272.
—— propionyl-, 272.
Rhamnodulcite, 39.
Ridge cultivation, 822.
Robiquet's method for detecting salicylic acid in urine, 748.
Rock of the St. Gothard Tunnel, 366.
Roman chamomile oil, acids obtained by the saponification of, 454.
—— —— —— constituents of, 454.
Rosaniline, 384, 385.
—— group, colouring matters of the, 236, 787.

Rosaniline, influence of metatoluidine in the preparation of, 625.
—— diazohydrocyanopara-, hydrochloride of, 385.
—— hydrocyanopara-, 385.
Rosanilines, constitution of, 463.
Rose, garden, ash of the, 338.
Rosemary, essence of, 725.
—— essence of, action of sulphuric acid on, 726.
—— essence of, oxidation of, 726.
—— oil, preparation of, 97.
Roseo-chromium compounds, 124.
Roseocobalt hydrate, 598.
—— nitrate, 598.
Rosin, testing of beeswax for, 283.
—— oil, hydrocarbon from, 467.
Rosolic acid, 386.
—— acids, 59.
Rye, ripening of, 337.

S.

Saccharic acid, action of phosphorus pentachloride on, 917.
—— —— dry distillation of ammonium salts of, 524.
Saccharine matter contained in vines suffering from the phylloxera, 1049.
—— substances and compounds, improvement in the preparation and treatment of, 423.
—— —— or compounds, improvement in the treatment of, 421, 496.
Saccharite, 360.
Safrosin, manufacture of, 292.
Saki, the alcoholic drink of the Japanese, 413.
Saleritin, glucoside of, 1038.
Salicylamide, α-nitro-, and its salts, 381.
—— β-nitro-, 382.
Salicylates and their application, 641.
Salicylic acid as a preventative of house-fungus, 1080.
—— —— α-acetamido-, and its salts, 381.
—— —— α-amido-, 381.
—— —— detection and estimation of, in animal secretions, 488.
—— —— detection of, in beer, 343.
—— —— diazo-, 928.
—— —— dimetanitro-, and its salts, 382.
—— —— in urine, Robiquet's method for detecting, 748.
—— —— iodo-, 928.
—— —— meta-iodonitro-, 928.
—— —— α-nitro-, and its salts, 380.
Salicylic acid, β-nitro-, and its salts, 381.
—— —— parahydroxy-, 928.
—— —— parazosulphoxylbenzene-, 316.
—— —— reaction of, with ferric salts, 748.
—— acids, iodo-, 928.
—— —— nitro-, 928.
Salicylo-sulphuric acid, α-amido-, 381.
Saline solutions, vapour-tension and solidifying points of, 4.
Saliva, test for nitrates in, 630.
Salt solutions and attached water, 428.
Salts, action of acids on, 689.
—— compounds of, with compound ammonias, 376.
—— influence of substitution on evolution of heat during the formation of, 767.
—— metallic, decomposition of, and certain inverse reactions which take place in presence of water, 1006.
—— —— galvanic properties of solutions of, 863.
—— of the earth-metals, fluorescence of, 862.
—— preparation of, in a finely-divided state, 107.
Saltpetre, Chili, as a manure for barley, 1051.
—— South American, 1073.
Samarium, a new metal from samarskite, 889.
Samarskite, a new metal from, 889.
—— of N. Carolina, probable existence of a new metal in, 116.
Sandal wood, colouring matter of, 470.
Santonine, absorption-spectra of, in solution, 269.
—— colour reaction with antimony trichloride, 832.
Santonin derivatives, 331.
—— monobromometa-, 330.
—— two isomerides of, 330.
Sap of *Carica Papyra*, action of, 1048.
Sarracenia Purpurea, 541.
Sausages, estimation of starch in, 979.
Scandium, 601.
Scapolites, presence of chlorine in, 697.
Scheelite, didymiferous, artificial production of, 696.
—— estimate of cerite metals in, 696.
Scopolia Japonica, 333.
Sea water, action of, on iron and steel plates, 564.
—— —— air contained in, 1060.
—— —— carbonic anhydride in, 1061.
—— —— presence of ammoniacal salts in, 9.
Sebacic acid, aniline derivatives of, 376.
Sebanilic acid, 377.
Sebanilide, 377.

Seed, choice of beetroot for, 822.
—— of *Sorghum vulgare*, analysis of, 956.
Seeds, influence of temperature on the germination of, 393.
—— of *Lallemantia iberica*, 822.
Selenates of magnesium metals, volume constitution of, 768.
Selenious acid, specific gravity of, 691.
—— oxide, specific gravity of, 691.
Selenium, absorption of, by plants, 955.
—— action of, on metallic sulphides, 771.
Seleniocyanates, 35.
Sericite rocks of the Taunus, 23.
Sericite-gneiss in the Bündener Alps, 25.
—— —— or phyllite, 207.
Serpentine from Verrages (Aosta), 362.
Shave-grass, analysis of, 956.
Shea- or Ghea-butter, 568.
Sheep, digestion in the different divisions of the digestive canal of, 391.
—— fattening of, 811.
—— feeding experiments with, 951.
Silent electric discharge, 435.
Silica, absorptive power of, 339.
—— gelatinous, an inorganic membrane, 199.
Silicated carbon filters, experiments with, 986.
Silicates containing fluorine, behaviour of, at high temperatures, 772.
Siliceous pig-iron, preparation and use of a highly, 678.
Silicium chloride, heat of vaporisation of, 767.
—— —— specific heat of, 767.
—— hydride, liquefaction of, 436.
Silicon, estimation of, in pig-iron and steel, 974.
—— chloride, action of sulphuric monochloride on, 201.
—— hydride, decomposition of, by electric spark, 767.
—— —— heat of formation of, 767.
Silicon-iron, remarkable specimen of, 204.
Silk, raw, influence of the chemical composition of the water used in the preparation of, 493.
—— cocoons, analysis of, 952.
Silver, estimation of, by ammonium thiocyanate, 973.
—— extraction of, from fahl-ores, 755.
—— spitting of, 438.
—— and other metals, extraction of, from pyrites, 288.
—— assay, use of Hempel's lamp for illustrating, as a lecture experiment, 402.
—— bromide, action of light of different colours on, impregnated with various organic colouring matters, 504.
Silver bromide, amount of bromine substituted by chlorine in, 770.
—— chloride, action of light on, 694.
—— phosphide, 508.
—— sulphide, action of selenium on, 771.
—— —— from Andreasberg, 898.
—— ultramarine, 437.
—— and iron, sulphide of, from Andreasberg, 440.
Sinistrin, 779.
Slate, composition of, 1024.
Soaps and alkaline resinates, abnormal solubility of certain bodies in, 99.
Soda, assimilation of, by plants, 666.
—— improvements in the manufacture of, 422.
—— industry, 677, 751.
—— Solvay's, used in the preparation of ultramarine, 987.
Soda-fusion process, formation of cyanogen compounds in, 751.
Soda-lyes, estimation of cyanogen in, 402.
Sodium, action of, on sodium hydroxide, 689.
Sodium amalgam, action of dilute hydrochloric acid on, 864.
—— —— action of water on, 864.
—— anthracenesulphonate, 653.
—— bromide, action of chlorine on, 770.
—— —— action of oxygen on, 770.
—— carbonate, dihydrated, 194.
—— carboxytartronate, 643, 644.
—— chloride, blue flame from, 497.
—— dinitro-dioxyquinone, 644.
—— hydrate, action of the vapour of, on red hot iron, 887.
—— hydrosulphide, heat of formation of, 865.
—— —— heat of hydration of, 865.
—— hydroxide, action of sodium on, 689.
—— nitrite, action of, on blood, 817.
Sodium-nitrobutylene, 701.
—— oxide, action of hydrogen on, 689.
—— —— heat of hydration of, 689.
—— sulphate, anhydrous, heat developed by contact of water with, 589.
—— —— anhydrous, preparation of, from Glauber salt, 596.
—— —— monohydrated, 194.
—— sulphides, heat of formation of, 865.
—— —— heat of hydration of, 865.
—— sulpho-pyroterebate, preparation of, 187.
—— sulpho-ricinoleate, preparation of, 187.

Sodium-thioacetanilide, action of ethyl bromide on, 312.
—— —— action of monochloracetic ether on, 313.
Soil, constancy and variation in the composition of, 666.
—— exhaustion of, by beet-root cultivation, 1050.
—— formation of nitrites in, 737.
—— greenstone, of Berneck, 824.
Soils, absorptive power of, 339, 552, 667.
—— cohesive power of, 957.
—— heat-capacity of, 958.
—— influence of, on the decomposition of organic substances, 339.
—— mechanical analysis of, 673.
—— of vine growing districts of the Rhine and Maine, analysis of, 737.
—— temperature of, 824.
Solanidine, composition of, 541.
—— acetyl-, 541.
Solanine and the products of its decomposition, 541.
—— acetyl-, 541.
Solar chemistry, recent researches on, 425.
—— spectrum, cause for the appearance of bright lines in, 574.
—— —— presence of dark lines in, which closely correspond with the lines of the spectrum of oxygen, 997.
—— —— region of the, indispensable to vegetable life, 336.
—— —— ultra-violet, limit of, 861.
Solid bodies, expansion of, 1002.
Solidifying point of saline solutions, 4.
Soluble blue, 418.
Solutions of metallic salts, galvanic properties of, 863.
—— supersaturated, 501.
Solvay's soda used in the preparation of ultramarine, 987.
Sorbite, action of phosphorus pentachloride on, 917.
Sorgho or Dhurra grass, cultivation of, 823.
Sorghum saccharatum, cultivation of, 823.
—— *vulgare*, cultivation of, 823.
Specific gravities, determination of, 498.
—— gravity, determination of, 197.
—— —— determinations, 295, 1004.
—— —— determinations of solid organic compounds, 610.
—— —— of powdered substances, determination of, 669.
—— heat of ethyl silicate, 767.
—— —— of silicium chloride, 767.
—— —— of water, 1002.
Spectra, absorption-, 101.
Spectra, absorption-, of didymiferous minerals, measurement of, 697.
—— —— difference in absorption, 1, 189.
—— of gases, influence of temperature and pressure on, 101.
—— of solutions of brucine, morphine, strychnine, veratrine, and santonine in concentrated acids, 269.
—— of the elements and their compounds, 685.
—— of vapours and gases, influence of temperature and pressure on, 685.
—— photographed, of oxygen and hydrogen, 497.
—— researches on, 575.
Spectroscope, new universal stand for use with the pocket-, 574.
Spectroscopic investigation of the constitution of liquids, 101.
Spectrum, absorption-, of alizarin and of some colouring matters derived from it, 807.
—— —— of nitro-alizarin, 807.
—— —— of pseudopurpurin, 807.
—— —— of purpurin, 807.
—— analysis, quantitative, 828.
—— continuous, of the electric spark, 765.
—— displacement of the lines of, by the motion due to the sun's rotation, 574.
—— of didymium nitrate, 861.
—— of erbium nitrate, 862.
—— of oxygen, 861.
—— —— presence of dark lines in the solar spectrum which correspond closely with the lines of, 997.
—— of ytterbium, 861.
—— solar, ultra-violet limit of, 861.
Spergulin, a new fluorescent body, 469.
Spiegeleisen, changes which it undergoes when smelted, 841.
—— specific heat of, 840.
Spinelle in dolerite, from Ovifak, 894.
—— of Tiriolo in Calabria, 694.
Spirit, potato, preparation of pressed yeast as a bye-product from, 843.
Spongy iron filters, experiments with, 986.
Sporadosidereal meteorites, metallic granules of, 609.
Squill, a new carbohydrate from the, 779.
Stand, new universal, for use with the pocket spectroscope, 574.
Standard weights and measures, material for, 102.
Stannamyl iodides, 919.
Stannic oxide, solubility of, in hydrochloric acid, 888.
—— phenyl chloride, action of nitrous acid on, 651.

Stannisopropyls, 918.
Stannobutyl iodides, 919.
Stannodiethyl compounds, crystalline form of, 518.
Stannodiphenide diethoxide, 250.
Stannodipropyl compounds, crystalline form of, 519.
Stannodipropyl oxide, 519.
Stannophenyl chloride, 651.
—— chloride, synthesis of, 249.
—— chloriodide, synthesis of, 250.
—— chlorobromide, synthesis of, 250.
—— dibromide, synthesis of, 250.
—— diiodide, synthesis of, 250.
—— oxide, synthesis of, 249.
Stannophenylhydroxyl chloride, synthesis of, 249.
Stannopropyl, iodides of, 622.
Stannopropyls, 918.
Stannotriethyl compounds, crystalline form of, 519.
Stannotrimethyl sulphate, crystalline form of, 519.
Stannotriphenyl chloride, 250.
Stannous chloride, vapour-density of, 1014.
—— oxide, crystalline, preparation of, 1016.
Starch, action of diastase, saliva, and pancreatic juice on, 370.
—— estimation of, in sausages, 979.
—— formation of, in chlorophyll grains in absence of light, 551.
—— granules of the egg, 662.
—— in paper, quantitative estimation of, 180.
—— modifications of the physical properties of, 518.
—— tenacity of, 570.
Steam, decomposition of bones by, 987.
—— superheated, 838.
—— boilers, heating, 1070.
—— —— wearing of, 410.
Steel, a third form of carbon in, 842.
—— chrome-, 286, 287.
—— chrome-crucible, preparation of, 567.
—— crucible, manufacture of, 1076.
—— direct preparation of from iron ores, 409.
—— direct process for making, 565.
—— estimation of silicon in, 974.
—— gases in, 437.
—— mild, working of, 410.
—— presence of nitrogen in, 1017.
—— specific resistance of, 1000.
—— thermo-electric position and electric conductivity of, in their relation to its hardness, 999.
—— plates, action of sea water on, 564.
—— welding, 567.
Steeling copper plates, 186.
Stilbene, colour reaction with antimony trichloride, 831.
Stillbite, 606.
Stokes's law of fluorescence, 862.
—— law of fluorescence, S. Lamansky on, 862.
Stone of the "Julius Column," 25.
Stoneware-clay, analysis of, 87.
Strontia, action of chlorine on, 596.
Strontium, existence of, in all rocks of the primary formation, 444.
—— bromide, action of oxygen on, 770.
—— chloride, action of oxygen on, 770.
Strychnine, absorption-spectra of, in solution, 269.
—— reaction with antimony trichloride, 832.
—— researches on, 387.
—— dihydro-, 387.
—— trihydro-, 387.
Stützite, 898.
Styceric or phenylglyceric acid, 644.
Substitutions, heat effect of, 871.
Succinic acid, dibromo-, reaction of, with water, 523.
—— —— iso-, synthesis of, 783.
—— —— tribromo-, 373.
—— fermentation, 394.
Succinyl compounds of toluidines, 461, 527.
—— relations of tetric acid and its homologues to, 459.
Sugar, action of heat on, 911.
—— —— potassium or ammonium dichromate on, 911.
—— as a test of the purity of water, 1062.
—— beet-, influence of light on the yield of, 1047.
—— cane-, fermentation of, 336.
—— —— inversion of, 336.
—— —— inversion of, and consecutive alteration of the glucoses so formed, 369.
—— crystallisation of, 844.
—— estimation of, in blood, 674.
—— estimation of, in malt liquors by the ammoniacal copper test, 1066.
—— hesperidin, 468.
—— improvements in the treatment of, 421.
—— inverted, estimation of, in presence of saccharose, 180.
—— —— influence of temperature on the deviation of polarised light by solutions of, 832.
—— —— preparation of, 187.
—— ratio of, in the beet to the phosphoric acid in the root and leaves, 818.
—— raw, analysis of, 404.
—— recovery of, from calcium saccharates, 492.

Sugar, recovery of, from molasses, 844.
—— transformation of, into alcohol, 778.
—— volumetric estimation of Pavy's process, 557.
—— candy, preparation of, 844.
—— solutions, action of heat on, 911.
Sugars, 449.
Suint from wool, utilisation of, 86.
Sulphaminemesitylenic acids, 643.
Sulphates, action of hydrochloric acid gas on, 105.
—— double, action of hydrochloric acid gas on, 105.
—— of magnesium metals, volume-constitution of, 768.
—— researches on, 104, 593.
Sulphides, alkaline, dissolved, heat of formation of, 866.
—— —— thermo-chemical studies of, 865.
—— metallic, action of organic solvents on, 771.
—— —— action of selenium on, 771.
—— —— dissociation of, 13.
—— —— heat of formation of, 433.
—— new application of rapid oxidation by which, are utilised for fuel, 755.
Sulphobenzide, action of sulphuric hydroxychloride on, 243.
—— tetranitro-oxy-, and its salts, 244.
Sulphobenzide-disulphonic acid, 649.
Sulphobenzide-monosulphonic acid, 649.
Sulphobenzide-sulphonic acid, 243.
Sulphochlorides, action of, on amines, 920.
Sulphones, aromatic, synthesis of, 242.
—— of the olefine series, 37.
Sulphonic compounds, preparation of, from diazo-compounds by means of sulphurous acid, 933.
Sulphoparatoluamide, 639.
Sulphoparatoluic acid, 638.
Sulphoselenium oxytetrachloride, 201, 691.
Sulpho-titanium oxytetrachloride, 691.
Sulphotoluide, constitution of, 926.
Sulphur, action of organic solvents on, 771.
—— estimation of, in the ore, fuel, and products of the iron industry, 974.
—— extracted from cast-iron by ether or petroleum, 771.
—— extraction of, by means of superheated steam, 284.
—— in fossil resin, 896.
—— production of, from sulphurous acid and hydrogen sulphide, 1012.
—— quantitative determination of, in illuminating gas, 78.
—— separation of, in open hearth, puddling furnace, and Bessemer converter, 185.
Sulphur, solubility of, 104.
—— use of carbon bisulphide for the extraction of, 837.
—— vapour-density of, 767.
—— oxygen and the halogens, reciprocal displacements between, when combined with hydrogen, 296.
—— oxytetrabromide, experiments on the preparation of, 354.
Sulphuretted hydrogen, preparation of, 1013.
—— —— preparation of, for chemico-legal investigations, 671.
—— —— use of, in the dry way in analysis, 963.
Sulphuric acid, behaviour of nitrogen acids with, 770.
—— —— detection of, in wine, 981.
—— —— manufacture, loss of nitre in, 838.
—— —— waste, improvements in treating, that has been used for pickling iron plates and other articles of iron or steel, 423.
—— anhydride, action of aluminium chloride on, 620.
—— bromide, experiments on the preparation of, 354.
—— dichloride, 200.
—— monochloride, 200.
—— —— action of, on the chlorides of titanium, antimony, tin, and silicon, 201.
—— —— boiling point of, 691.
—— —— mode of action of, 229.
Sulphurous acid, action of hydrogen sulphide on, in presence of salts, 1012.
—— —— and hydrogen sulphide, production of sulphur from, 1012.
—— anhydride, action of, on aluminium chloride, 915.
Superphosphate, insoluble phosphoric acid in, 1052.
—— bone-meal, manure experiments with, 959.
—— —— estimation of soluble phosphoric acid in, 672, 745.
—— estimation of the value of, 967.
—— retrogradation of, 987.
Supersaturated solutions, 501.
Syenite-porphyries of South-west Norway, 362.
Sylvanite, 897.
Synanthrose, 337.
Syntonin, 489.
Syrup, beet-root, purification of, 844.
Szaboite, a new mineral, 441.

T.

Table of reduction of weighings in air to a vacuum, 396.
Tacca pinnatifida, examination of, 860.
Tan-liquors, estimation of free acid in, 980.
Tane-koji, preparation of, 413.
Tannic acid, improvements in the manufacture of materials containing, 496.
Tannin estimation, Gerland's process for, 933.
—— extraction of, from wine, 1078.
—— synthetical, 645, 646.
—— and allied substances, certain reactions with, 160.
Tanning, 100.
—— mineral, 100.
Tannins, phloroglucin-, detection of, 979.
Tar distilleries, extinguishing fire in, 1080.
Tartaric acid, formation of glycollic and pyruvic acids from, 916.
—— —— free, detection of, in wine, 981.
—— —— pure, preparation of, 917.
—— —— test to distinguish it from citric acid, 674.
Taurine, methyl-, 225.
Taurocyamine, 226.
—— methyl-, 226.
Tea, average composition per cent. of, 856.
—— Chinese, examination of, 851.
—— detection of iron salts in, 854.
—— examination of, 558.
—— test for catechu in, 854.
—— test for logwood in, 854.
Teak wood, 996.
Teeth, analysis of alloys used as stopping for, 1076.
Tellurium ores of Siebenbürgen (Transylvania), 897.
Tellursilberblende, a new species, 898.
Temperature, influence of, on the deviation of polarised light by solutions of inverted sugar, 832.
—— influence of, on the evolution of carbonic anhydride by barley seeds, 1048.
—— influence of, on the spectra of vapours and gases, 685.
—— of soils, 824.
—— surrounding, influence of, on the tissue change of warm-blooded animals, 951.
Terbium and its compounds, 114.
—— formate, 114.
—— oxide, 113, 602.
—— sulphate, 114.
Terebenthene, derivatives of, 328.
—— dihydrochloride, action of sodium on, 944.
Terebenthene hydrochloride, liquid and solid, 328.
Terephthalic acid, 638.
—— —— hydroxy-, 793.
—— —— methoxy-, 793.
—— —— monobromo-, 639.
Terpene, Russian dextrogyrate, from the turpentine of *Pinus silvestris*, 168.
—— hydrochlorides, 943.
—— di-isoprene and caoutchene, identity of the hydrates of, 1039.
Terpenes, compounds of, with hydrochloric acid, 943.
—— hydration of, 726.
—— structure of, 167.
Terpinol, 944.
Terpinylene, 944.
Tetra-ammoniacal hydrochloride, 501.
Tetrachlorazoxybenzide, 231.
Tetrallylammonium bromide, 779.
Tetramethylammonium ferricyanide, 611.
α-Tetramethylbenzene derivatives (durene), 713.
Tetramethyldiamidobenzophenone, 921.
Tetramethyldiamidodiphenylmethane, 921.
Tetramethyldiamidotriphenylmethane, 236.
Tetramethylethylene and its derivatives, 536.
Tetramethylparaphenylenediamine, 627.
Tetramethyltriamidotriphenylmethane, reduction of, 788.
Tetraphenylethane, 68, 318.
—— tetrahydroxyl-, 69.
Tetraphenylethane sulphonic acid, 69.
Tetraphenylethylene, 318.
Tetrapyridine, 732.
Tetrathionic acid, 1013.
Tetrazone, 451.
Tetrethylammonium ferricyanide, 612.
Tetrethyltetrazone, 451.
Tetric acid and its homologues, 457.
—— —— and its homologues, relation of, to succinyl, &c., 459.
Tetrolic acid, synthesis of, 782.
Tetroxydiphenol, 634.
Teucrin, 728.
Teucrium fruticans, 728.
Thallium tellurate, specific gravity of, 1004.
Thaumasite, a new mineral species, 21.
Thebaïne, colour reaction with antimony trichloride, 831.
Theobromine, quantitative determination of, in cacao and chocolate, 406.
Thermal effect of the walls of closed vessels on the contained gases, 432.
Thermic constants of diamylene, 874.
—— —— of glycerol, 874.

Thermic researches on ethyl silicate, 767.
Thermo-chemical relation between the boiling and melting points of solid elements, 690.
—— —— results, accuracy of, 433.
—— —— studies of the alkaline sulphides, 865.
Thermochemistry, combination of carbonic oxide with the elements, 591.
Thermodynamics, relation between work effected by the diffusion of gases and the second law of, 3.
Thermoelectric position and electric conductivity of steel in their relation to its hardness, 999.
Thermometry, researches in, 588.
Thialdine, action of potassium permanganate on, 710.
—— formula of, 711.
Thiamides of monobasic organic acids, 922.
—— of the oxalic acid series, 784.
Thioacetic acid, ethereal salts of, 786.
Thioaldehyde, 452.
—— action of potassium permanganate on, 710, 711.
Thioacetanilide, action of methyl iodide on, 313.
—— allyliso-, boiling point of, 786.
—— ethyliso-, action of, on aniline, 786.
—— —— action of oxalic acid on, 786.
—— —— boiling point of, 786.
—— isobutyliso-, boiling point of, 786.
—— isopropyliso-, boiling point of, 786.
—— methyliso-, boiling point of, 786.
—— propyliso-, boiling point of, 786.
Thiobenzaldehyde, 791.
—— action of potash on, 791.
Thiobenzyl ether, benzimido-, 923.
Thiocarbamide, angelyl-, 712.
—— dibutyl-, 713.
—— monophenyl-, preparation of phenylcyanamide from, 804.
—— sulphine compounds of, 650.
—— tertiary butyl-, 713.
Thiocarbamides, action of iodine on, 48.
—— aromatic, 804.
Thiocarbimide, amido-, 806.
—— angelyl-, 712.
—— anilido-, 806.
—— chlorophenyl-, 805.
—— —— hydrochloride, 805.
—— hydroxyphenyl-, 805.
—— orthotolyl-, action of chlorine on, 935.
—— phenyl-, action of, on diphenyl guanidine, 804.
—— —— action of phosphorus pentachloride on, 805.
—— tertiary amyl-, 713.
Thiocarbimide, tertiary butyl-, 713.
—— tolyl-, 935.
Thiocarbimides, action of phosphorus pentachloride on, 805.
Thio-derivatives, 786.
Thiodiethyloxamide, 784.
Thiodiglycollic ether, 138.
Thioethyl ether, benzimido-, 922.
—— —— phenylacetimido-, 922.
Thioglycollic ether, 138.
Thiohydantoïn, nitroso-, and its salts, 712.
Thiophenol, action of sulphuric monochloride on, 229.
—— chloronitro-, 231.
Thiotetrapyridine and its salts, 732.
Thirlmere, analysis of the waters of, 906.
—— water of, 211.
Thomsonite, occurrence of, at Läven, 605.
Thonstein, 208.
Thymolic acid, 158.
Thymoloxycuminic acid and salts of, 158.
Tiglic acid, 222.
—— —— action of bromine on, 456.
—— —— action of hydrobromic acid on, 455.
—— —— constitution of, 456.
—— —— conversion of angelic acid into, 454.
—— —— from Roman chamomile oil, 454.
—— and angelic acids, separation of, 455.
Time, influence of, on manuring in beet cultivation, 825.
Tin, grey modification of, 888.
—— occurrence of, in silicates, 608.
—— chloride, action of sulphuric monochloride on, 201.
—— phosphides, 509.
—— and lead alloys, behaviour of, with vinegar, 990.
Tissue change, influence of the surrounding temperature on, of warm-blooded animals, 951.
Titanium chloride, action of sulphuric monochloride on, 201.
Titration, use of phenol-phthaleïn in, 273.
—— use of tropæolin in, 176.
Tolidine sulphate, 236.
Tolidines (diamido-ditolyls), isomeric, 235.
Tolu-anisaldehydine, 234.
Toluene, action of sulphuric monochloride on, 229.
—— anhydro-valeryldiamido-, 312.
—— azo-derivatives of, 237.
—— bromo-, oxidation of, 320.

Toluene, compounds of aluminium chloride with, 308, 461.
—— meta-azo-, 236.
—— meta-hydrazo-, 236.
—— metanitro-, 236.
—— —— presence of, in commercial nitrotoluene, 625.
—— pentabromo-, 142.
Toluenedisulphamide, 804.
Toluenedisulphonic acid, 804.
Toluenedisulphoxide, 243.
Toluenemetasulphamide, Beckurts', oxidation of, 804.
Toluenemetasulphonic acid, Beckurts' so-called, 804.
Toluneorthosulphamide, 804.
Toluenesulphinic acid, action of fuming nitric acid and of nitrous acid on, 314.
Toluenesulphonic acid from diazo-compounds, 933.
Toluenesulphonic chloride, liquid, 804.
—— —— liquid, action of ammonia on, 804.
Tolufurfuraldehydine, and salts of, 234.
Toluic acid, *a*-oxypara-, and its salts, 323.
—— —— uronitro-, 815.
Toluide, metanitro-paratrichloraceto-, action of hydrogen on, 311.
—— metanitro-paravaleryl-, action of hydrogen on, 311.
Toluidine hydrochloride, heat of formation of, 871.
—— metanitro-para-, 311.
—— methylated derivatives of, and the colours obtained therefrom, 310.
—— succinyl-compounds of, 461.
Toluidines, succinyl-compounds of, 527.
Toluylenediamine hydrochloride, 311.
—— ortho-meta-, 232.
Toluylsuccinimide, 461.
Tolylarsenic acids, ortho- and para-, 163.
Tolylarsenious chloride, ortho- and para-, 163.
—— tetrachlorides, ortho- and para-, 163.
Tolylarsenoxides, 163.
Tolyldiphenylcarbinol, 386.
Tolyldiphenylmethane, 386.
Tolylenediamine, benzenylortho-, 715.
—— ethenyl-, 716.
—— ortho-, derivatives, 715.
—— para-, and its salts, 715.
Tolylphosphorus chloride, 721.
Tolylsuccinamic acids, 527.
Tolylsuccinamides, 527.
Tolylsuccinimides, 527, 528.
Topaz, behaviour of, at high temperatures, 772.
Triallylamine, 780.
Triamidotriphenylmethane, hexmethylated, 236.
Tribromoresorquinone, reduction of, 55.
Tricarbopyridenic acid, 541.
Trichlorobutylidenimide, 42, 452.
Trichlorovalerolactamide, or trichloroxyvaleramide, 41.
Trichlorvalerolactic or trichloroxyvaleric acid, 42.
Tricrotonylenamine and its salts, 780.
Tricyanic chloride, 517.
Tridymite, crystal system of, 358.
—— optical properties and crystalline form of, 605.
Triethylazonium iodide, 450.
Triethylbenzene, 785.
Triethyldicarbopyrrolamide, 525.
Triethylnaphthylphosphonium iodide, 68.
Triglycollic acid, 930.
Tri-isobutylamine, boiling point of, 704.
Trimethylamine, action of, on monochlorhydrin, 1031.
—— commercial, 912, 913.
—— sulphocarbamate, 305.
Trimethylcarbamine, 40, 141.
—— and its salts, 713.
Trimethyldiamidotriphenylmethane, 237.
Trimethylene bromide, conditions under which it is formed, 908.
Trimethyl-glycerammonium, chloride of, 1031.
Trinitroresorcinol, 603.
Trioxyanthraquinones, 942.
Trioxybenzene, ether-sulphuric acid of, 149.
Triphenylacetic acid, 326, 385.
Triphenylacetonitril, 385.
Triphenylarsine and its derivatives, 162.
Triphenylbenzene, perchlorination of, 721.
Triphenylcarbinol, trinitro-, 384.
Triphenylmethane, 326, 384.
—— colour reaction with antimony trichloride, 831.
—— chloride, 384.
—— cyanide, 326.
—— trinitro-, 384.
Triphylite, chemical composition of, 695.
Triploidite, 20.
Tritolylarsine, 163.
Tritungstates, 600.
Tropæolin, use of, in titration, 176.
Tropic acid, chlorhydra-, 720.
—— —— derivatives of, 720.
Tropide, 720.
Tropidine, preparation of, 733.
Tropine tropate, action of hydrochloric acid on, 733.
Tungstates of the earthy and metallic sesquioxides, 355.
Tungsten chlorides, 888.

Tungsten oxychlorides, 888.
Turkey-red dyeing, mordant for, 187.
—— —— oil, 187.
—— —— oil, analysis of, 984.
Turpentine, action of iodine on, 623.
—— formula of, 168.
—— French oil of, hydration of terpene from, 726.
—— Russian, hydration of terpene from, 726.
Turpentine-oil, action of hydrochloric acid on, 943.
Turquoise, detection of natural and artificial, 209.
Tyroleucine, 544.
Tyrosine, decomposition of, by putrefaction, 541.
—— obtained by the action of baryta on albumin, 544.

U.

Ulmin, 603.
Ultramarine, 506, 597, 885.
—— blue, 108, 110, 506.
—— constitution of, 203, 204, 1014.
—— green, 108.
—— potassium, 692.
—— red, 111, 506, 885.
—— silver, 437.
—— Solvay's soda used in the preparation of, 897.
—— violet, 111, 506.
—— white, 109.
—— yellow, 112, 885.
Ultramarines, organic, 329.
—— —— formation of, 622.
Ultra-violet limit of the solar spectrum, 861.
Umbelliferone, 720.
—— acet-, 721.
—— derivatives, 720.
—— methyl-, 721.
Undecylenic acid, conversion of, into undecylic acid, 306.
Undecylic acid, conversion of undecylenic acid into, 306.
Unghwarite, 31.
Uramil, synthesis of, 375.
Uranium, atomic weight of, 688.
—— nitrate, absorption spectra of, 189.
—— ore of Joachimsthal, vanadium from, 989.
—— pitchblende from Joachimsthal, 18.
Uranoso-uranic oxide, specific heat of, 688.
Uranyl ammonium selenite, 507.
—— bromide and its salts, 508.
—— potassium selenate, 507.
—— potassium selenite, 507.
Uranyl, some new salts of, 507.
Urea, estimation of, 985.
—— estimation of, by means of sodium hypobromite, 405.
—— estimation of, in urine, 1067.
—— formation of, in the animal organism, 952.
—— preparation of, from blood by alcoholic dialysis, 950.
—— researches on, contained in the organs, 175.
Urethane, orthamidophenyl-, 921.
—— orthonitrophenyl-, 921.
—— hydrochloride, orthamidophenyl-, 921.
—— —— orthamidophenyl-, action of potassium nitrite on, 922.
Uric acid, dimethyl-, 48.
—— —— derivatives, synthesis of, 375, 460.
—— —— formula, 142.
—— —— group, compounds of, 461.
Urine, detection of ethyldiacetic acid in, 560.
—— detection of indican in, 343.
—— estimation of chlorine in, 830.
—— estimation of nitrogen in, 829.
—— estimation of urea in, 1067.
—— of herbivorous animals, source of hippuric acid in, 952.
—— Robiquet's method for detecting salicylic acid in, 748.
Urobilin, 170.
Uronitrotoluic acid, 176.

V.

Valeramide, trichloroxy-, or trichlorovalerolactamide, 41.
Valeric acid, bromo-, 618.
—— —— dibromo-, action of alkalis on, 521.
—— —— hydroxy-, 45.
—— —— inactive (isobutylformic acid) and its salts, 139.
—— —— monochloro-dibromoxy-, 42.
—— —— trichloroxy-, or trichlorvalerolactic acid, 42.
Valerolactide, 140.
Valonia and certain other sources of tannin, 248.
Vanadium from the uranium ore of Joachimsthal, 989.
Vanillin in Siam benzoïn, 245.
Vanillo-diacetonamine and its salts, 144. 145.
Vapour-densities of certain high-boiling organic compounds, 1025.
—— —— of some metallic chlorides, 1013.

Vapour-densities, limits to the application of the method of determining, in the barometric vacuum, 499.
—— —— of some inorganic compounds, 875.
—— —— process for determining, 294.
Vapour-density at a high temperature in a vacuum, 197.
—— —— determination of, 177.
—— —— determination, modified, 196.
—— —— determinations at high temperatures of substances which attack mercury, 499.
—— —— determinations of inorganic bodies at high temperatures, 766.
—— —— of alizarin, 1039.
—— —— of ammonium dihydrosulphide, 880.
Vapours, influence of temperature and pressure on the spectra of, 685.
—— magnetic rotatory power of, 577.
Vapour-tension saline solutions, 4.
Varec, estimation of iodine in, 1051.
Vartry water, some peculiarities of, and its action on boiler-plates, 85.
Vedovine, a tannin extract, 496.
Vegetable life, region of the solar spectrum indispensable to, 336.
Veratrine, absorption-spectra of, in solution, 269.
—— colour reaction with antimony trichloride, 832.
Verryken's method of detecting metallic poisons, 973.
Vinasses, distillation of, 913.
Vine disease, 821.
Vinegar, behaviour of tin and lead alloys with, 990.
Vines, saccharine matter contained in, suffering from the phylloxera, 1049.
Viscosity a cause of catalysis, 876.
Vitellin, vegetable, 272.
Vitriol manufacture, loss of nitre in, 838.
Voltaic action, theory of, 426.
—— element with constant current, 426.
—— polarisation, capacity of, 864.
Volume-constitution of the sulphates, selenates, and chromates of the magnesium metals, 768.
Volumetric estimation of oxygen in water, Schutzenberger's process, 77.
Vyrnyw, analysis of the water of the, 906.

W.

Wagnerite from Bamle, in Norway, 441.
Water, absorption of, by leaves, 819.
—— analysis, 963.
Water attached, and salt solutions, 428.
—— Bohr's colorimetric process for the examination of, 553.
—— distance between the molecules of, 194.
—— distilled, preparation of, free from ammonia, 878.
—— electrolysis of, 577.
—— estimation of nitric acid in, 274.
—— evaporation of, from the ground, 667.
—— ferric chloride as a purifier of, 1072.
—— for brewing, analyses of, 1078.
—— from the River Dart, 906.
—— influence of coloured light on the evaporation of, 863.
—— mineral, curious concretion balls derived from a colliery, 1024.
—— of St. Dunstan's well, Melrose, analysis of, 905.
—— of the mineral spring at Suhl, 516.
—— of the River Vyrnyw, analysis of, 906.
—— of Thirlmere, analysis of, 211.
—— potable, detection and estimation of ferrous acid in, 964.
—— —— occurrence of bacteria in, 817.
—— —— preservation of, 85, 1072.
—— —— sanitary notes on, 985.
—— softening magnesia-hard, 985.
—— specific heat of, 1002.
—— spongy iron and animal charcoal as materials for purifying, 343.
—— sugar as a test of the purity of, 1062.
—— thermal, of Termini Imerese, analysis of, 698.
—— used in Peruvian saltpetre works, analysis of, 1073.
—— Vartry, some peculiarities of, and its action on boiler-plates, 85.
—— well, at Grouville, composition of, 1072.
—— and methyl alcohol, heat-capacity of mixtures of, 688.
Waters, boiler feed-, analysis of, 273.
—— mineral, of Auvergne, 446.
—— natural, estimation of organic matter in, 976.
—— of Lake Thirlmere, analysis of, 906.
—— of the Cheliff, analysis of, 699.
—— of the Nile, amount of nitric acid in, 905.
—— well, inconstant composition of, 485.
Wax, Japanese, 1037.
—— of *Ficus gummiflua*, 261.
Weeds used as salad, analysis of, 821.
Weighings in air, reduction of, to a vacuum, 396.

Well-water at Grouville, composition of, 1072.
Well-waters, inconstant composition of, 485.
Weselsky's reaction for phloroglucin, 979.
Wheat, blighted, detection of, in flour by the spectroscope, 977.
—— disease, 820.
Whey, skimmed, composition of, 856.
Willow, chemical constituents of, and its pathological formations, 160.
Wine, adulteration of, 82.
—— apple, 1078.
—— changes which it undergoes when kept, 763.
—— clarifying and preserving, 290.
—— detection of free tartaric acid, and of sulphuric acid in, 981.
—— Dochnahl's new method of preparing, 569.
—— estimation of acetic acid in, 980.
—— estimation of alcohol and extractive matter in, 179.
—— estimation of glycerol in, 404.
—— extraction of tannin from, 1078.
—— fining of, 1078.
—— good, action of the ferment of sour wine on, 817.
—— pear, 1078.
—— plastering of, 681, 762.
—— red, colouring matter of, 171.
—— —— making, 681.
—— —— pressing of, 681.
—— sour, action of the ferment of, on good wine, 817.
Wines, amount of sulphuric acid in, 762.
—— detection of grape sugar in adulterated, 82.
—— new, time of first racking off, 569.
Wood, composition of, 613.
—— Quebracho, 996.
—— teak, 996.
Wood charcoal, absorbing power of, 761.
Wood gum, 613.
Wood spirit, estimation of methyl alcohol in, 487.
Wood vinegar, acids of, 43.
Wool dyeing, use of chrome alum instead of potassium dichromate in, 185.
Wort, effect of artificially manured barley on the composition of, 959.
Worts, beer, rotatory power of, 993.

X.

Xanthine derivatives, formation of, from albumin, 471.
Xanthinine, 784.
Xanthorhamnin, 39.
—— formula of, 271, 272.
Xylene, action of sulphuric monochloride, on, 229.
—— meta-, 623.
—— ortho-, separation of, from its isomerides, 919.
—— para-, 623.
—— sulphamido-, oxidation of, 52.
Xylenesulphamide, β-meta-, 62.
—— —— monobromo-, 62.
Xylenesulphonic acid, dibromo-meta-, 61.
Xylenes, formed by the action of aluminium chloride on methyl chloride and benzene, 228.
Xylenol, a solid, 641.
—— meta-, solid, 643.
Xylenols, homo-oxybenzyl alcohols, hydroxytoluic aldehydes, alcohol- and aldehyde- hydroxybenzoic acids, and hydroxyphthalic acids, relation between, 924.
Xylidide, aceto-para-, 52.
Xylidine, a new, 919.
—— acetyl α- and acetyl β-meta-, 157.
—— cobalt chloride, 461.
—— α- and β-meta-, 157.
—— α- and β-meta-, hydrochloride, 157.
—— α-meta-, nitrate, 157.
—— para-, and its salts, 51.
Xyloquinone dibromometa-, 530.

Y.

Yeast, artificial, for molasses distilleries, 1078.
—— beer-, lecithin and nucleïn in, 811.
—— composition of, 477.
—— preservation of, 817.
—— pressed, preparation of, as a bye-product from potato spirit, 843.
—— researches on, 476.
Yellow dolomite from Bleiberg, 19.
—— ultramarine, 885.
Ytterbia, 601, 602.
Ytterbium, a new metal from gadolinite, 118.
—— spectrum of, 861.
Yttrium chlorostannate, 602.
Yttrogummite, 365.

Z.

Zinc, action of water and saline solutions on, 11.
—— acetate, 452.

Zinc arsenates, 884.
—— chloride, vapour-density of, 1014.
—— estimation of, 672.
—— estimation of, available in zinc-dust, 400.
—— estimation of, by precipitation as oxalate, 1054.
—— improvements in the manufacture of sulphide and other compounds of, and in the production of bye-products resulting therefrom, 423.
—— new volumetric method for estimating, 1054.
—— phosphates, 1016.
—— phosphide, 508.
—— separation of ferric oxide and alumina from, 970.
Zinc, separation of, from nickel, 276.
—— separation of manganese from, 1055.
—— sulphide solution, electric conductivity of, 864.
—— sulphydrate, 206.
—— and nicotine, double chloride of, distillation of, with soda-lime, 809.
Zinc-dust, estimation of the available zinc in, 400.
Zinc-methyl, action of, on the bromides of monobrominated acid radicles of the *a*-series, 46.
Zircon crystals, twin, 363.
Zoisite, 606.
Zsadányer meteorite, analysis of, 397,

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ERRATA.

The asterisk in the second column indicates that the line is counted from the bottom.

Page.	Line.	Error.	Correction.
160	3	pyrocatechuic	pyrocatechin
,,	4	,,	pyrocatechyl
620	20*	their	thus
766	16	1	a'
768	15	275	2·75
815	1	sulphonic	quinolsulphonic
,,	6	phenolsulphonate	quinolsulphonate
816	1	evaporation	decomposition
,,	5	cooling	calving
817	6	treating	breathing
820	23*	*calvis*	*lævis*
,,	16*	plot A	plot 4
,,	10*	45 7 1	45 7 1 per cent.
821	4	plarmodium	plasmodium
,,	12	carried	caused
,,	25	Falchette	Falchetto
823	12*	130·1	13·01
828	19	308 lbs.	388 lbs.
858	2	1080·4	1030·4
,,	15*	of	on
843	13	the analyses of the 20 samples of beer were made by Scalweit	

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